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A STUDY
FOR
HYPERGOLIC VAPOR SENSOR DEVELOPMENT
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TITLE: A STUDY FOR HYPERGOLIC VAPOR SENSOR DEVELOPMENT

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TABLE OF CONTENTS

	PAGE
TABLE OF CONTENTS	i
LIST OF TABLES	ii
LIST OF FIGURES	iii
I. INTRODUCTION	1
II. EXPERIMENTAL	2
III. RESULTS AND DISCUSSIONS	7
A) THE MODEL 6601 MMH ANALYZER	7
B) THE MODEL 6302 NO ₂ ANALYZER	15
C) THE MODEL 7630 MMH/NO ₂ ANALYZER	22
D) ANALYSIS AND HANDLING OF HYPERGOLIC VAPORS	27
IV. CONCLUSIONS AND RECOMMENDATIONS	35
REFERENCES	38
APPENDIX I OPERATION OF THE HYDRAZINES DILUTION APPARATUS	39
APPENDIX II ANALYTICAL PROCEDURES FOR H, MMH, AND UDMH ANALYSIS	43

LIST OF TABLES

		PAGE
TABLE I	DESIGN GOALS: PORTABLE HYPERGOLIC VAPOR DETECTION SENSORS	3
TABLE II	OPERATING CONTROLS AND INDICATORS	9
TABLE III	INSTRUMENT SPECIFICATIONS	12
TABLE IV	INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS MODEL 6601 ECOLYZER	14
TABLE V	OPERATING CONTROLS AND INDICATORS	17
TABLE VI	INSTRUMENT SPECIFICATIONS	20
TABLE VII	INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS	21
TABLE VIII	MODEL 7630 MMH/NO ₂ ECOLYZER	23
TABLE IX	INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS	24
TABLE X	EFFECT OF 50 FT. OF TEFLON TUBING ON MODEL 7630 ECOLYZER S/N B-1282 PERFORMANCE	26
TABLE XI	HYDRAZINES DILUTION SYSTEM PERFORMANCE	29
TABLE XII	MMH, N ₂ H ₄ , AND UDMH STABILITY IN TEFLON	31
TABLE XIII	CALIBRATION OF MMH SENSORS BY ALTERNATE GAS EXPOSURE	33
TABLE XIV	VOLUME VAPOR NECESSARY FOR SPECIFIED ACCURACY USING COLORIMETRIC ANALYSIS	36

LIST OF FIGURES

- FIGURE 1 SCHEMATIC OF ELECTROCHEMICAL SENSOR
- FIGURE 2 POTENTIOSTAT AND SENSOR ELECTRODES
- FIGURE 3 MMH HIPSTER SENSOR RESPONST TO 7.7 PPM MMH/N₂
- FIGURE 4 SENSOR SIGNAL VS. FLOWRATE
- FIGURE 5 MMH HIPSTER
- FIGURE 6 MMH HIPSTER INTERNAL
- FIGURE 7 FLOW DIAGRAM OF THE MMH HIPSTER
- FIGURE 8 MMH RESPONSE FOR PROTOTYPE HIPSTERS B001 and B002
- FIGURE 9 LINEARITY STUDY FOR MMH HIPSTER
- FIGURE 10 TEMPERATURE DEPENDENCE OF MODEL 6601 ECOLYZER
- FIGURE 11 MMH PROBE ASSEMBLY
- FIGURE 12 INSTRUMENT RESPONSE TO 6.5 PPM MMH SAMPLE THROUGH PROBE
- FIGURE 13 NO₂ SENSOR RESPONSE TO 9.59 PPM NO₂
- FIGURE 14 NO₂ HIPSTER SENSOR FLOWRATE DEPENDENCE
- FIGURE 15 NO₂ HIPSTER
- FIGURE 16 NO₂ HIPSTER INTERNAL
- FIGURE 17 FLOW DIAGRAM OF THE NO₂ HIPSTER
- FIGURE 18 NO₂ RESPONSE OF PROTOTYPE HIPSTER A001
- FIGURE 19 TEMPERATURE DEPENDENCE OF MODEL 6302 ECOLYZER
- FIGURE 20 MODEL 6302 NO₂ ECOLYZER LINEARITY
- FIGURE 21 NO₂ PROBE ASSEMBLY
- FIGURE 22 SCHEMATIC DIAGRAM OF MODIFIED MMH 7000 SERIES PLUMBING
- FIGURE 23 MODEL 7630 MMH TEMPERATURE DEPENDENCE S/N 1282
- FIGURE 24 EFFECT OF TEFLON TUBING ON MMH RESPONSE
- FIGURE 25 EFFECT OF TEFLON TUBING ON NO₂ RESPONSE MODEL 7630 ECOLYZER
- FIGURE 26 UDMH/N₂ STABILITY
- FIGURE 27 COLORIMETRIC CALIBRATION CURVE FOR MMH
- FIGURE 28 COLORIMETRIC CALIBRATION CURVE FOR HYDRAZINE
- FIGURE 29 COLORIMETRIC CALIBRATION CURVE FOR UDMH

I. INTRODUCTION

This final report covers work performed under contract NAS 10-8982 for the period April 8 to October 8, 1977. The major effort has been to develop, design, fabricate and test portable electrochemical analyzers for monomethylhydrazine and NO₂ measurement. The objective of this report is to summarize the major findings of this work.

A prior report (1) details the electrochemical technology which was used to develop the fixed installation MODEL 7630 ECOLYZER. A similar approach has been taken in this program for the development of the portable instrumentation.

Additional effort was needed to improve the MODEL 7630 ECOLYZER for its field application and this work will be discussed.

In order to prepare this instrumentation for effective field implementation, instrument calibration and handling techniques were developed along with needed accessories.

In summary, the following tasks were completed within the scope of this work.

- TASK I: A portable MMH analyzer was developed, designed, fabricated and tested.
- TASK II: A portable NO₂ analyzer was developed, designed, fabricated and tested.
- TASK III: Sampling probes and accessories were designed and fabricated for this instrumentation.
- TASK IV: Improvements and modifications were made to the MODEL 7630 ECOLYZER in preparation for field testing.

TASK V: Instrument calibration procedures and hydrazine handling techniques necessary to the successful application of this hardware were developed.

The design goals for the portable instrumentation for NO₂ and MMH are given in TABLE I. The successful completion of these objectives was most easily accomplished using the commercially available 6000 Series ECOLYZER "Hipster" design. Therefore, to meet these goals a MODEL 6601 MMH ECOLYZER and a MODEL 6302 NO₂ ECOLYZER were developed.

The following report discusses the effort necessary to meet these instrument design objectives and successfully complete the major tasks of this work.

II. EXPERIMENTAL

The fundamental design of these instruments includes an electrochemical cell as the vapor detection principle. A complete description of this technique has been reported (1) and therefore only a summary of the experimental techniques used for development of the instrumentation is discussed here.

A schematic diagram of the electrochemical sensor design is shown in (FIGURE 1). The three electrodes are all Teflon-bonded diffusion electrodes prepared by spraying a catalyst-Teflon dispersion onto a hydrophobic Teflon film. The Platinum and Gold catalyst materials were purchased as high surface area powder. These electrodes were sealed to a polypropylene chamber which was subsequently filled with electrolyte. The aqueous electrolyte, was prepared from reagent grade materials and distilled and deionized water.

TABLE I
DESIGN GOALS
PORTABLE HYPERGOLIC VAPOR DETECTION SENSORS

Single Channel	MMH/hydrazine or NO₂
Ranges (switch select)	MMH - 0-2 ppm, 0-20 ppm NO₂ - 0-5 ppm, 0-50 ppm
Size	6" x 4" x 3"
Weight	3.5 pounds
Response Time (90%)	30 seconds
Recovery Time (90%)	30 seconds
Accuracy	± 2% F.S.
Reproducibility	± 2% F.S.
Noise	1% F.S.
Specificity	Specific for gas of interest
Zero and Span Drift	Below 10% F.S. over 30 days
Operating Temperature	32° - 104°F
Operating Humidity	5% - 100% RH
Continuous Operation	8 hours
Battery Recharge	16 hours

Gold and platinum leads from the sensor electrodes were attached to a potentiostat (FIGURE 2) and hydrazine sensing electrodes were potentiostatically controlled at +100 mV with respect to the Pt/air reference electrode while NO₂ sensing electrodes were controlled at -200 mV with respect to the sensor's Pt/air reference electrode. The reference electrode, Pt/air, was stable to $\pm 0.01V$ at approximately $1.0 \pm .030V$ in acid electrolyte with respect to the normal hydrogen electrode.

Hipster sensors were filled with 13.5 cc of electrolyte. The hydrazine cells used 23% KOH solution while the NO₂ cells used 28% H₂SO₄ solution as the electrolyte. All sensors for hydrazine analysis had Teflon faceplates.

During sensor evaluation, gas mixtures were passed over the back (gas) side of the sensing electrode at constant flowrate, typically 400 cc/minute, and the current produced by electrochemical reaction in the sensor flowing between the sensing and counter electrodes was monitored. The sensors currents were measured by monitoring the voltage drop across a precision resistor (typically 1K) in series with the sensing electrode and displaying this voltage on a strip chart recorder. Background currents were measured for the sensor in a "static" condition (no gas flow through the sensor) and in a dynamic or "steady state" condition i.e., with a constant gas flow of "zero" grade air (79% N₂, 21% O₂) through the sensor. Signals for the various gas mixtures were obtained by filling gas sample bags with the desired mixture and, by using an air sampling pump, drawing this gas into the sensor

at flowrates which were constant for each analysis. In this manner the sensor signal (current) was measured as the difference in sensor output at steady-state between zero air and the pollutant gas mixture.

A dynamic dilution apparatus was used to synthesize mixtures of Hydrazine, MMH, and UDMH in both N_2 and air. It consisted of a Sage Model 355 syringe pump which delivered liquid (neat) hydrazines through a septum-sealed port into the diluent gas stream. The system was all glass except for TFE valve stems. By adjusting the flowrate of diluent gas and hydrazine liquid, a variety of mixtures from < 1 ppm to > 100 ppm could be synthesized in a continuous fashion. These streams were collected in 50 liter Teflon sample bags which allowed several tests to be performed with the same homogeneous vapor mixture sample. For a detailed procedure for the operation of the dilution apparatus, see Appendix I.

Wherever possible available standard gas mixtures were obtained. For NO/N_2 , NO_2/air , H_2/air , CO/air , NH_3/N_2 , H_2S/N_2 , SO_2/air , and Freon-12/ N_2 samples, mixtures were obtained commercially at various ppm level concentrations while CO_2 , N_2 , O_2 and He were obtained as pure gases.

To obtain mixtures of these gases at intermediate concentrations, i.e., for linearity studies, a dynamic dilution scheme was used. It consisted of the pure gas or gas mixture and the diluent gas being continuously blended through two calibrated flowmeters ($\pm 1\%$). This allowed dilution mixtures over approximately one order of magnitude to be prepared with approximately $\pm 2\%$ precision.

In order to calibrate the hydrazine analyzer, it is important to know accurately the hydrazine concentration. Due to the special problems involved in preparation of hydrazines vapor mixtures it was necessary

to develop precise procedures for vapor mixture analysis. Colorimetric methods were developed for the determination of hydrazine, MMH, and UDMH vapor in air or nitrogen by modifying previously existing methods. The exact procedures used in vapor mixture calibration are detailed in Appendices II-A, II-B, and II-C for MMH, hydrazine, and UDMH, respectively.

The sampling method employed involved direct collection of the vapor mixtures by trapping them in a midget impinger apparatus. Hydrazine vapors were collected in 0.1 N HCl, MMH vapors in 0.1 N H₂SO₄ and UDMH vapors in a citric acid/Na₂HPO₄ buffer solution.

The analysis of aqueous samples of hydrazine and MMH consisted of reacting the N₂H₄ or MMH with p-dimethylaminobenzaldehyde to form a yellow dye. Since UDMH does not form a dye with p-DMAB, another analysis was used which involved reacting the UDMH with trisodium-dimethylamino-pentacyanoferrate and analyzing the resultant red solution colorimetrically. All colorimetry was performed with a Bausch and Lomb Spectronic 20, using a wave length of 457 nm for N₂H₄ and MMH and 500 nm for UDMH. Standard solutions of H, MMH, and UDMH were prepared gravimetrically from the appropriate salts of the hydrazine compounds.

A Tenney Environmental Chamber was used to evaluate the instrument performance specifications under varying environmental stresses.

III. RESULTS AND DISCUSSIONS

For the purpose of clarity, this section of the report is divided into four discussions.

- A. The Model 6601 MMH Analyzer
- B. The Model 6302 NO₂ Analyzer
- C. The Model 7630 MMH/NO₂ Analyzer
- D. Analysis and Handling of Hypergolic Vapors.

In each of these discussions the results of the test program will be discussed.

A. The Model 6601 MMH Analyzer

The initial phase in the development of this instrument was the construction and evaluation of the electrochemical sensor. This transducer is the heart of the instrument analyzer since within it the electrochemical analysis of the hydrazine occurs.

The "hipster" sensors described in Section II were selected for prototype instrument development. They exhibited a typical background current of 2 μA and a sensitivity to MMH of approximately 13 $\mu\text{A ppm}^{-1}$. This indicates a background signal equivalent to approximately 150 ppb. Initial sensors had a rise time of 50 seconds to 90% of signal and a decay time 30 seconds to 90% of signal when tested at 7.7 ppm MMH and 400 cc min⁻¹ of sample gas flow. A typical response is shown in FIGURE 3 where the arrows indicate exposure of the sensor to the MMH/N₂ mixture and then exposure to room air. The initial signal from the sensor is nearly instantaneous while the attainment of steady-state occurs only after several minutes.

The response of this sensor was measured at various flowrates between 0 and 700 cc min⁻¹ for MMH/N₂, N₂H₄/N₂ and UDMH/N₂ vapor mixtures with the results shown in FIGURE 4. The concentration of MMH was approximately 13.8 ppm while the concentration of N₂H₄ was approximately 8.8 ppm and the concentration of UDMH was approximately 6.6 ppm. All the flow dependencies are similar and indicate that 400 cc min⁻¹ or higher is a suitable flowrate for instrument operation. It is noted that the sensor signal for the most volatile of the hydrazines, UDMH, is least sensitive to flow above 400 cc min⁻¹. It was observed that all of the hydrazines gave well behaved, repeatable steady-state signals at the flowrates studied.

Subsequent to this initial sensor functional test, this sensor design was incorporated into the 6000 Series ECOLYZER instrument. A picture of the resulting analyzer is shown in FIGURE 5. By reference to TABLE II the control functions of the instrument can be understood. Three instruments were fabricated in the design and identified as S/N B001, B002 and Prototype II. The instruments were designed to operate in the range 0-2 and 0-20 ppm MMH. FIGURE 6 illustrates how the instrument separates for service revealing the internal structure and layout. The major components from left to right contained in the top half are the Teflon sample intake, pump, panel meter and electronics and the lower half contains from left to right the audible alarm, the sensor and the rechargeable battery pack.

The instrument's three basic functional sections; the sensor, the pump system and the electronic system are illustrated schematically in

TABLE II
OPERATING CONTROLS AND INDICATORS

INDEX NUMBER	CONTROL OR INDICATOR	FUNCTION
1.	Gas level meter	Indicates the level of pollutant in parts per million (ppm).
2.	Span Adjustment	Used to adjust the detector calibration when performing calibration procedure.
3.	Zero Adjustment	Used for the precise setting of the instrument zero.
4.	Alarm Set	Used to set the level at which the audible alarm will activate.
5.	"ON" Light	Illuminates to show pump is activated.
6.	"LOW BATT" Light	Illuminates when battery voltage is low.
7.	Probe and Filter Assembly	Used to sample ambients and remove particulates.
8.	OFF/L/H Switch	Turns pump on and off selects range.
9.	Alarm "ON/OFF" Switch	Used to silence audible alarm.
10.	Charging Receptacle (Located on bottom)	Used for receiving plug from connector.
11.	Recorder Jack	Display gas level on recorder trace.
12.	Gas Exhaust	Used to divert sampled gas stream away from user. (Hydrazine only).

FIGURE 7. The pump draws the sampled vapor mixture through the intake and into the electrochemical sensor at a constant flowrate. The sensor then analyzes the vapor mixture producing an electric current which is proportional to the concentration of hydrazine in the vapor mixture. The electronics serve to control the sensor during analysis and amplify the output for display and alarm.

Representative responses at room temperature are shown in FIGURE 8 for 7.4 ppm of MMH in N₂. The circles mark the 90% rise and decay points and these are within 30 seconds of vapor mixture exposure. This response was more rapid than initial sensor testing since flowrates for these instruments were typically greater. This will reduce effects due to adsorption and reaction of the vapor mixture prior to its analysis in the instrument sensor. The precision of these analyses was $\pm 1.5\%$ and both precision and response times were found to be improved at higher concentrations. At levels below 1 ppm MMH response times of several minutes to 90% of signal was observed with precisions of $\pm 3\%$ to $\pm 10\%$.

The instrument response was determined for several MMH concentrations and the result is shown in FIGURE 9. The concentrations of MMH was determined colorimetrically by the method given in Appendix II with an accuracy of $\pm 5\%$. The instrument is linear in MMH concentration within the experimental uncertainties in the measurements. The noise level on these particular instruments was less than 10 ppb MMH.

Studies of the effects of temperature upon the performance of the ECOLYZER instrument for hydrazine analysis were carried out in an environmental chamber. At temperatures below 10°C, water vapor and hydrazine

vapors condensed in the instrument intake tubing and it was very difficult to obtain accurate and representative results. Special precautions were taken, to utilize only dry gas mixtures and exclude room air from the environmental chamber and the MODEL 6601 intake. The results of these experiments are reported in FIGURE 10. The instrument output (FIGURE 10A) exhibits a span variation of 38% over the entire region of 2-40°C or approximately 1%/degree centigrade. This effect can be minimized by electronically compensating for this span change and, indeed, this approach has proven successful in this type of electrochemical instruments for CO, NO, and NO₂. Instrument zero changes (FIGURE 10B) of ± 100 ppb are observed using this instrument but this poses little problem since the instrument can easily be zeroed in the field immediately prior to vapor measurements.

The zero and span drift measurements are complicated since there is a simultaneous time dependence for zero and span drift occurring along with the temperature measurements. The zero drift of an intermittently operated MSH hipster was 0.02 ppm over a period of 11 days and the span drift was 1.4% over the same period. On another MSH hipster 0.06 ppm was observed for zero drift over 10 days. These drifts are necessarily included in the reported temperature measurements.

From the descriptive instrument data collected using the three prototype instruments, we have developed the general instrument specification reported in TABLE III. By comparison with TABLE I (INTRODUCTION) we note that the design goals of the program have been achieved.

TABLE III
INSTRUMENT SPECIFICATIONS

	MODEL 6601 MMH HIPSTER
Charging Power Requirements	110V to 120V AC, 50/60 Hz
Charging Time	16 hours
Operating Time with Full Charge	8 hours
Standby Power Consumption	<48 hours
Ranges (Dual)	0-2/0-20 ppm MMH
Accuracy	± 5%
Reproducibility	± 1.5%
Response Time (90% Rise, Decay)	36 seconds
Noise	1% F.S.
Stability	
Zero Drift	± 2% F.S. per day
Span Drift	± 2% of range per day
Temperature Drift	0°C - 40°C
Humidity Range	5% - 95% R.H.
Dimensions	3" x 5" x 8"
Weight	3.5 pounds

In any field use one of the most important characteristics of an instrument is its selectivity or discrimination. This is the ability to detect the toxic vapor of interest in the presence of other atmospheric constituents. The interference due to selected pollutants for this hydrazine sensor are given in TABLE IV. The major interferences are found to be NH_3 , NO_2 , and the sulphur gases H_2S and SO_2 . The normal constituents of ambient air namely N_2 , O_2 , CO and CO_2 are not reactive with this sensor and therefore do not interfere with the vapor analysis.

Hydrazine vapors in air or nitrogen pose a special problem in analysis. The nature and the area of the surfaces which are in contact with the vapors have an extensive effect on the vapor mixture stability. Therefore, the design of this instrument includes fittings and plumbing of FEP and TFE Teflon wherever the vapor mixture to be analyzed is in contact with the instrument. In order to sample specific locations at a distance from the instrument intake, a remote sampling probe was designed and constructed as shown in FIGURE 11. It is a protectively sleeved Teflon tube with connecting fittings on each end. One fitting is designed to insert into the MMH Hipster instrument intake while the other fitting mates with a Teflon probe designed to be hand-held and sample locally. The probe itself has multiple recessed vapor inlets at the tip to avoid the possibility of clogging and also a Teflon screen particulate filter built into the handle.

A prototype probe was constructed and evaluated with the result shown in FIGURE 12. The response of the Hipster is shown for 6.5 ppm MMH with the 14 foot Teflon probe attached to the instrument inlet. The response is

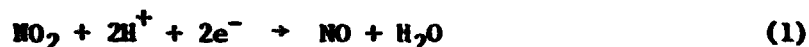
TABLE IV
INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS
MODEL 6601 ECOLYZER

GAS MIXTURE	READINGS DUE TO INTERFERENT ON MMH HIPSTER IN PPM	INTERFERENCE RATIO PPM INTERFERENT = PPM MMH
6 ppm MMH	6.,	1:1
9.59 ppm NO ₂	-0.7,	14:1
107 ppm H ₂	0.01,	11000:1
89.8 ppm CO	0.26,	345:1
2030 ppm CH ₄	0.05,	40600:1
111 ppm NH ₃ (Max. Peak)	31. ,	4:1
24.6 ppm NO	0.07,	350:1
20.3 ppm SO ₂	3.2 ,	6:1
30.4 ppm H ₂ S	29. ,	1:1
10 ⁶ ppm N ₂	0.0 ,	>10 ⁸ :1
10 ⁶ ppm O ₂	0.04,	>10 ⁷ :1
10 ⁶ ppm He	0.04,	>10 ⁷ :1
10 ⁶ ppm CO ₂	5.0 ,	2x10 ⁵ :1
1013 ppm Freon-12	0.16,	6300:1

the same magnitude as the instrument without the probe except a slightly longer approach to steady-state signal is observed. This means that calibration of the instrument without the probe, will not cause error in the field when sampling with a probe. However, it is recommended to calibrate with the probe in place since this will also insure proper probe performance.

B. THE MODEL 6302 NO₂ ANALYZER

This instrument development was based upon Energetics Science, Inc's gas monitoring technology (2, 3) and the recent development of the MODEL 7630 ECOLYZER (1). The instrument transducer operates by sensing NO₂ vapors electrochemically. The electrochemical reaction at the sensing electrode is:



while the reaction at the counter electrode is:



This yields an overall cell reaction of



for this sensor. Under the conditions of cell operation this reaction or sensing mechanism is highly selective. Similar to the previously described hydrazine transducer, this cell is constructed from three Teflon-bonded diffusion electrodes in the "Hipster" design.

The sensors selected for evaluation exhibited typical background currents of 1-2 μA and a sensitivity of approximately 3 $\mu\text{A}/\text{ppm}^{-1}$. A typical sensor response is shown in FIGURE 13. The speed of sensor response is dependent upon both the cell electrode batch from which the transducer was fabricated and also upon the concentration. Sensor rise

time decreases at increasing concentration providing faster measurement at the more dangerous levels. Responses were less than 30 seconds to 90% of signal even for the slowest cells at the low concentrations.

The sensor signals were then measured at flowrates between 0 and 1.1 l min^{-1} with the result shown in FIGURE 14. The cell signal becomes less sensitive to flowrate changes as the flowrate increases. In this case the cell will be operated above 1 l min^{-1} and therefore should exhibit virtually no changes in the output signal with minor fluctuations in the instrument flowrate.

The cells were fabricated into the prototype Hipster instruments for evaluation. A picture of the resulting analyzer, the ECOLYZER MODEL 6302 NO_2 Hipster is shown in FIGURE 15. In FIGURE 16 the internal construction and layout is illustrated. The major components from left to right are: pump, panel meter, and electronics in the upper case half and audible alarm, electrochemical cell, and battery pack in the lower case half. In TABLE V the operating controls and indicators are listed. Three instruments were fabricated and identified as S/N A001, A002, and prototype VI. The instruments were designed to operate in the ranges 0-5 and 0-50 ppm NO_2 with switch selectable ranging.

The instrument's basic functional components are shown in FIGURE 17 consisting of pumping system, electrochemical cell, and control and display electronics. The pump pushes a sample through the electrochemical cell where the vapors are analyzed and an output proportional to the NO_2 concentration is produced. This output signal is displayed on the instrument

TABLE V
OPERATING CONTROLS AND INDICATORS

INDEX NUMBER	CONTROL OR INDICATOR	FUNCTION
1.	Gas level meter	Indicates the level of pollutant in parts per million (ppm).
2.	Span Adjustment	Used to adjust the detector calibration when performing calibration procedure.
3.	Zero Adjustment	Used for the precise setting of the instrument zero.
4.	Alarm Set	Used to set the level at which the audible alarm will activate.
5.	"ON" Light	Illuminates to show pump is activated.
6.	"LOW BATT" Light	Illuminates when battery voltage is low.
7.	Probe and Filter Assembly	Used to sample ambients and remove particulates.
8.	OFF/L/H Switch	Turns pump on and off selects range.
9.	Alarm "ON/OFF" Switch	Used to silence audible alarm.
10.	Charging Receptacle (Located on bottom)	Used for receiving plug from connector.
11.	Recorder Jack	Display gas level on recorder trace.
12.	Gas Exhaust	Used to divert sampled gas stream away from user. (Hydrazine only).

panel meter directly in ppm NO₂ or can be recorded using the 0-1V recorder output provided.

Representative responses of the NO₂ Hipster instruments are shown in FIGURE 18. The circles indicate 90% of sensor response and these are all within 30 seconds of initial gas mixture exposure. The precision for these instruments was $\pm 1\%$ at concentrations in the 0-50 ppm region while the precision on the 0-5 ppm scale was typically $\pm 1.5\%$. Noise levels were 0.05 ppm or lower corresponding to less than 1% of full scale on the most sensitive operating range. Complete and accurate analysis for NO₂ is accomplished with this instrument in less than two minutes.

In FIGURE 19 the dependence of the instrument output at temperatures between 0 and 40°C is reported. A total span change of less than 15% is observed over the range 0-40°C or approximately 0.3% per °C and normal temperature fluctuations in ambient conditions are compensated. Typical zero changes of 0.2 ppm or 4% of full scale on the most sensitive range are shown in FIGURE 19 over the temperature range 0-40°C. As is observed, the instrument zero exhibits only a slight dependence upon the temperature of operation. Both the span signals and the zero signals reported here have been compensated by installation of electronic compensation circuitry within the instrument.

The response of the instrument was measured at concentrations between 0 ppm and 10 ppm with the result shown in FIGURE 20. The linearity of the instrument was within the experimental error of the gas mixture with which the measurements were made.

The instrument specifications resulting from consideration of these measurements are given in TABLE VI. This summarizes the instrument characteristics and illustrates that the program design goals (TABLE I) have been achieved.

The specificity of this instrument has been evaluated and the result is expressed in TABLE VII. The major interference is found for SO₂ gas mixtures however, no interference is recorded for the normal constituents of ambient air.

A probe assembly described in FIGURE 21 was designed to interface with this instrument during ambient sampling. No effect upon instrument response was produced by attachment of the probe assembly. The probe contains an in-line interference filter for field monitoring. This filter removes particulates and protects the instrument sensor. The probe is designed with several sampling ports at the tip so that it cannot be easily plugged and is fabricated from a single piece of polypropylene. Vinyl tubing is used to connect the probe tip to the instrument intake.

TABLE VI
INSTRUMENT SPECIFICATIONS

ITEM	MODEL 6302/NO ₂ HIPSTER
Charging Power Requirements	110V to 120V AC, 50/60 Hz
Charging Time	Overnight (approx. 16 hours)
Operating Time with full charge	Eight (8) hours of continuous operation
Standby Power Consumption	No more than 48 hours between charge and use
Standard Ranges (Dual)	NO ₂ 0-5 ppm/0-50 ppm
Response Time	90% of signal within 30 sec.
Accuracy	± 2% of full scale range
Reproducibility	± 2% F.S.
Noise	< 1% F.S.
Stability	
Zero Drift	± 2% of full scale per day
Span or Calibration	± 2% of range per day
Operating Temperature (for full accuracy)	32°F - 104°F
Operating Relative Humidity Range	5% to 95% R.H.
Physical Dimensions	3" x 5" x 8"
Weight	3.5 lbs.

TABLE VII
INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS

GAS MIXTURE	READING DUE TO INTERFERENT IN PPM ON NO₂ HIPSTER	INTERFERENCE RATIO PPM INTERFERENT = PPM NO₂
6 ppm MMH	- 0.02	300:1
9.59 ppm NO ₂	9.6	1:1
107 ppm H ₂	- 0.05	2140:1
89.8 ppm CO	- 0.01	8980:1
2030 ppm CH ₄	- 0.06	33833:1
111 ppm NH ₃ (Peak Max.)	- 0.1	1110:1
24.6 ppm NO	- 0.15	164:1
20.3 ppm SO ₂	-18.	1:1
30.4 ppm H ₂ S	- 0.06	507:1
10 ⁶ ppm N ₂	- 0.07	10 ⁶ :1
10 ⁶ ppm O ₂	0.15	>10 ⁶ :1
10 ⁶ ppm He	- 0.15	>10 ⁶ :1
10 ⁶ ppm CO ₂	0.0	NO INTERFERENCE
1013 ppm Freon-12	0.0	NO INTERFERENCE

C. THE MODEL 7630 MMH/NO₂ ANALYZER

The MODEL 7630 MMH/NO₂ ANALYZER was developed and as a continuous monitor for MMH and NO₂ in a fixed installation. The details of development and design have been reported (1). The performance characteristics of this instrument are summarized in TABLES VIII and IX.

The two prototype instruments, S/N 1261 and 1282, after having been fabricated and tested at Energetics Science, Inc., were submitted to the Naval Research Laboratory, Washington, D.C. for evaluation. As a result of this evaluation several design modifications were suggested. Consultations with the Kennedy Space Center Technical Program Director regarding further specific KSC requirements suggested further design change in these instruments. The following tests were carried out to implement these redesign features and to evaluate their effect upon instrument performance.

The pumping system in the instrument was evaluated to be inadequate for extended periods of operation. It was therefore removed and the alternate pumping system shown in FIGURE 22 was installed. This MMH system incorporates the same pump as the NO₂ analyzer section except that it is now located downstream from the electrochemical sensor. The tubing is fabricated from all Teflon parts from the sample intake to the sample exhaust from the sensor. The flow is adjusted through the sensor at 400 cc min⁻¹ allowing the remaining flow to exit through the system bypass. In this manner the intake sampling rate is maintained at 1.5 l min⁻¹ while the analysis is performed in the electrochemical sensor using on a fraction of the vapor mixture.

TABLE VIII
MODEL 7630 NH₃/NO₂ ANALYZER

	<u>NH₃ ANALYZER</u>	<u>NO₂ ANALYZER</u>
Multi-ranges	0-2, 0-20, 0-200 ppm	0-5, 0-50, 0-500 ppm
Minimum Detectable Sensitivity	20 ppb	50 ppb
Rise Time 90%	90 seconds	<30 seconds
Fall Time 90%	45 seconds	<30 seconds
Zero Drift*	±10%/30 Days	±10%/30 Days
Span Drift*	±10%/30 Days	±10%/30 Days
Precision	2% F.S.	2% F.S.
Accuracy¹	5% F.S.	2% F.S.
Noise	<1% F.S.	<1% F.S.
Operating Temperature Range	0-35°C	0-35°C
Operating Relative Humidity	10-95%	10-95%
Dimensions	← 8" x 8" x 16" →	
Weight	← 17 lbs. - 7.7 Kg. →	
Readout	Meter, 50 Divisions Mirrored Recorder, 0-5V DC	Meter, 50 Divisions Mirrored Recorder, 0-5V DC
Power	← 105 - 125V AC →	

*** Estimate**

1. Using a reference standard gas mixture of the same accuracy. With a more accurate standard reference method an accuracy within the specified precision can be achieved.

TABLE IX
INTERFERENCE EQUIVALENTS OF SELECTED POLLUTANTS

Gas Mixture	Reading Due to Interferent - PPM	
	H ₂ S Analyzer	NO ₂ Analyzer
NH ₃ 5 ppm/N ₂	5	-0.0
NO ₂ 5 ppm/Air	-0.3	5
H ₂ 23,400 ppm/Air	+4	-1.35
CO 248 ppm/Air	+0.25	-0.1
CO ₂ * - - -	0.0	0.0
CH ₄ 1000 ppm/N ₂	0.00	0.00
NH ₃ 111 ppm/N ₂	+40	-0.00
C ₂ H ₄ 2.27 ppm/N ₂	+0.1	0.0
N ₂ 10 ⁶ ppm	0.0	0.0
O ₂ ±100,000 ppm/N ₂	0.0	±0.015
Ar* - - -	0.0	0.0
He 10 ⁶ ppm	0.06	0.0
Freon TF (60% EtOH Azeotrope) 1000 ppm/N ₂	+0.2	0.0

* Estimate

The effect of this change upon instrument performance at various temperatures was evaluated. Since the NO₂ section of the instrument was not changed it was not included in these measurements and only the MMH channel of the instrument was evaluated. The results of the evaluation are shown in FIGURE 23. In FIGURE 23A the span change after room temperature calibration (23°C) is approximately 18% up to 35°C and 18% down to 2°C. This corresponds to 0.8 to 1.3% span change per °C. In FIGURE 23B the dynamic zero is shown as a function of the temperature. The instrument output is for the most sensitive range where 0-5V is equivalent to 0-2 ppm MMH. The total variation in zero is approximately 400 mV or 0.16 ppm MMH over the range of 2°C to 35°C.

These fixed installation instruments are designed to be used with a fifty foot sampling line and, therefore, require the ability to rapidly draw a sample through a 50 foot length of sample hose and perform an analysis. After several joint experiments with the Naval Research Laboratory, both ESI and NRL concluded that the sampling tube would be constructed of FEP Teflon. A fifty foot length of three sizes of Teflon tubing was evaluated for the sampling system. The comparison of the results for 1/8" O.D., 3/16" O.D., and 1/4" O.D. Teflon tubing is summarized in TABLE X. The size of the tubing has a marked effect on the flow and the pressure at the instrument intake. At these flowrates, however, the theoretical purge time (tube volume ÷ flowrate) is acceptable for all three types of tubing. The critical consideration is the effect of the tube upon the ECOLYZER performance. In FIGURES 24 and 25 the results are given for the MMH sensor and the NO₂ sensor, respectively. These results are summarized in TABLE X.

TABLE X

**EFFECT OF 50 FT. OF TEFLON TUBING ON MODEL 7630 ECOLYZER S/N B-1282
PERFORMANCE**

	NO TUBING	TUBING OUTER DIAMETER		
		1/4"	3/16"	1/8"
Instrument Intake Flow (cc/min)	1420	1270	1100	870
Pressure Drop (torr)	0	5	20	66
Theoretical Purge Time (sec)	0	12.7	6.7	4.7
MMH SENSOR RESPONSE				
Time to 1st Indication (sec)	0	18	12	6
$\Delta mV/ppm$ (5.7 ppm MMH)	230	211	211	202
90% Rise (sec)	80	120	90	84
90% Decay (sec)	30	72	60	50
NO₂ SENSOR RESPONSE				
Time to 1st Indication (sec)	0	18	9	4
$\Delta mV/ppm$ (9.59 ppm NO₂)	100	100	100	98
90% Rise (sec)	18	48	36	30
90% Decay (sec)	12	40	24	30

The time to first indication of the vapor mixture is rapid although different from the theoretical purge time. The 1/8" tubing was judged less acceptable since it had an effect of approximately 2% upon the NO₂ instrument span and 6% on the MSH instrument span. The 3/16" tubing minimized this span change while at the same time maintained a rapid signal rise and decay time characteristic. Therefore, 3/16" FEP Teflon is the best choice tube of those tested for use as a 50 foot sampling probe.

Other modifications made to the instrument included changing the intake and exhaust fittings to 3/16" Teflon compression fittings, pinning these fittings in the housing to avoid slippage; modification of the sensor endplate to accommodate the new plumbing designs, modification of the chassis to accommodate the new internal layout design and temporary securing of the circuit cards. The instruments were then thoroughly examined and calibrated before delivery to Kennedy Space Center for field test evaluation.

D. ANALYSIS AND HANDLING OF HYPERGOLIC VAPORS

One of the most essential phases in the development of new technology is the development of a successful implementation scheme for the technology. In the case of the hypergolic vapors, this requirement is for laboratory calibration procedures, field functional testing and field calibration.

For the NO₂ (N₂O₄ vapor) detectors, calibration is accomplished in the laboratory or in the field using commercially available NO₂/AIR gas mixtures. Since these come in a variety of sizes, a suitable sample for field use is available. During calibration or sensor functional testing, the gas mixture is dispensed from the cylinder into a 5 liter Teflon gas

sample bag. This sample bag is then attached to the instrument intake fitting via a calibration bag adapter and the instrument draws the sample into the sensor and performs the analysis. By having a knowledge of the NO_2 gas mixture concentration, usually supplied as $\pm 2\%$ accuracy, the analyzer can be calibrated.

Energetics Science, Inc. has developed a zero air filter which is capable of removing electrochemically active gases from an ambient air stream. This device is 4" long and 3/4" in diameter and can interface with any ECOLYZER analyzer. This allows the operator to zero the instrument in the laboratory or in the field simply by attaching the filter to the analyzer intake. This procedure is recommended for the Model 7630F, the Model 6601, and Model 6302 ECOLYZERS for instrument zero adjustments.

The calibration of the MMH analyzer requires the generation and analysis of H, MMH and UDMH vapor mixtures and their analysis by a standard analytical technique.

Vapor mixtures of Hydrazine, Monomethylhydrazine, and Unsymmetrical-dimethylhydrazine were prepared in a dynamic dilution system. This dilution system and its operation are described in Appendix I and Section II (EXPERIMENTAL) of this report.

The performance of this dilution system was evaluated by collecting a variety of samples over the course of several months of operation and analyzing them colorimetrically. The theoretical concentration was calculated by assuming a 95% purity for the starting hydrazines and measuring the liquid and N_2 gas diluent delivery rates. A summary of the result is shown in TABLE XI. The efficiency of impinger vapor sample collectors was also

TABLE XI
HYDRAZINES DILUTION SYSTEM PERFORMANCE

Syringe Pump Settings 60% $\frac{1}{1000}$

10 μ l Syringe 700 cc/min N₂

VAPOR	THEORETICAL CONCENTRATION	COLORIMETRIC CONCENTRATION	EFFICIENCY OF DILUTION SYSTEM	EFFICIENCY OF COLLECTION @ 475 cc/min
MMH	9.4 ppm	4-9 ppm	38-96%	99.8%
N ₂ H ₄	14.9 ppm	4-11 ppm	27-74%	99.8%
UDMH	6.2 ppm	2-5 ppm	32-81%	95%

evaluated by placing an electrochemical sensor on the output of the impinger. The collection efficiency is 95-100% while the dilution system efficiency can vary between 27 and 96%. Therefore it is extremely important to perform a colorimetric analysis of the vapor mixture prepared in the dilution apparatus before it is used for instrument calibration.

After generation, these vapor mixtures were trapped in Teflon sample bags and then they were analyzed using an electrochemical sensor. The results are given in TABLE XII. The vapors exhibit greater stability in nitrogen than in air in these Teflon vessels and in general the order of stability can be given as UDMH > MMH > H at the 5 ppm level. In FIGURE 25 the stability of UDMH in N₂ is shown over an extended time. In this test a 50 liter Teflon vapor sample bag was filled with approximately 8 ppm UDMH/N₂ and analyzed using an electrochemical sensor at various times. Since the stability of the UDMH mixture is good showing only 5% decay over 48 hours this would be a mixture stable enough to be transported short distances for field calibration of the hypergolic instrumentation. When mixtures of H or MMH are used for instrument calibration, they should be prepared and analyzed as they are used.

We have evaluated several alternate methods for field calibration of the MMH analyzer. One used a glass container with a semipermeable membrane housing containing neat Hydrazine. A second was a sealed polypropylene housing filled with a solution of H, MMH or UDMH in contact with a porous Teflon membrane. Both of these techniques exhibited instability in the liquid phase over relatively short (5-day) time intervals. These methods were, therefore, judged inadequate for the construction of field calibration

TABLE XII
MMH, N₂H₄, AND UDMH STABILITY IN TEFLON

GAS MIXTURE	PERCENT DECOMPOSITION AFTER 30 MINUTES	
	IN NITROGEN	IN AIR
~ 5 ppm MMH	2.4%	7%
~ 5 ppm N ₂ H ₄	11 %	24%
~ 5 ppm UDMH	0 %	0%

devices. Similar performance was found for a standard hydrazine permeation device.

A third approach to field calibration of the MMH analyzer was evaluated, namely, the signal due to an alternate reactive gas is used as a measure of the sensor activity for hydrazine. For such a scheme to be successful, the alternate gas must be a measure of the catalytic activity of the electrochemical cell for hydrazine oxidation. Such a dependence would not be easily predicted but could be present in this type of chemical system. The results of this evaluation are given in TABLE XIII. The results show that the electrochemical cell activity toward NO_2 and H_2S exhibits similar characteristics to the cell activity for MMH. The other gases studied in the ppm region show no obvious correlation. The $\text{H}_2\text{S}/\text{MMH}$ activity ratio is $1.08 \pm 16\%$ and the NO_2/MMH activity ratio is $9.6 \pm 4\%$. The NO_2 signal was negative making this measurement not easily read on the instrument meter output without additional electronic modification. None of the gases tested were judged acceptable for instrument calibration but $\text{H}_2\text{S}/\text{N}_2$ gas mixtures could provide a convenient field functional test gas for this instrument. Hydrogen sulphide gas mixtures prepared in nitrogen are commercially available.

The activity of the MMH sensor for all the hydrazines i.e., H, MMH, and UDMH was measured. The signals were characterized using both 6000 Series and 7000 Series sensors. A knowledge of this activity will allow one to calibrate the instrument for either H, MMH or UDMH and by application of an appropriate scale factor obtain an accurate measurement for each of these vapors. The Hipster 6000 Series instrument when calibrated for MMH will be calibrated for H by multiplying the observed MMH readings by 1.1

TABLE XIII
CALIBRATION OF MMH SENSORS BY ALTERNATE GAS EXPOSURE

		ALTERNATE GAS/MMH				7-28-77
CELL #	HFS-35-A	HFS-21	H-MMH-7	H-MMH-18	H-MMH-19	
SO ₂	2.83	Gave no signal -----				
H ₂ S	0.817	0.92	1.14	1.06	1.45	

$$\overline{\text{H}_2\text{S/MMH}} = 1.08 \pm 16\%$$

		ALTERNATE GAS/MMH		9-6-77
CELL #	HFS-41	HFS-47	H-MMH-16	
NO	97.3	92.3	34.1	
CO	4280	1030	233	
H ₂	864	545	1690	
NH ₃	8.79	22.6	4.25	
NO ₂	-10.2	-9.03	-9.60	

$$\overline{\text{NO}_2/\text{MMH}} = 9.64 \pm 4.2\%$$

and will be calibrated for UDMH by multiplying the observed MMH readings by 1.4. The 7000 Series instrument will require a calibration factor of 1.1 for H and 1.6 for UDMH. These calibration factors are accurate to $\pm 15-20\%$ at present and are applicable in the linear range of these instruments. Drift and temperature characteristics of these analyses have not been completely verified but as more sensors and instruments are fabricated, this cross-calibration factor will be refined to $\pm 10\%$ (the limit of this refinement will be approximately $\pm 5-10\%$). It can then be certified for each instrument and allow accurate field measurement of all the hydrazines with only a single calibration.

The prior discussions of instrument performance have relied upon a suitable method for instrument calibration. Therefore, considerable effort was used to develop a reference technique for hydrazine analysis. The methods examined included direct chromatographic detection, derivatization gas chromatography, stain tube analysis, titration methods, and colorimetry. Of these techniques, the colorimetric method was selected for further development (4).

Calibration curves were determined for the colorimetric methods given in Appendices II A, B, and C using the $N_2H_4 \cdot (HCl)_2$ and $MMH \cdot H_2SO_4$ salts which were quantitatively diluted to ppm and sub-ppm levels in acid solutions, and neat UDMH which was diluted in a buffer solution. The results are given in FIGURES 26, 27 and 28 for H, MMH, and UDMH, respectively.

Vapor samples from the dilution system were prepared for analysis by collection in a midjet impinger. The details of the procedure used for each type of vapor are outlined in Appendices II A, B, and C. Typically 3 to 5 liters of vapor mixture was passed through the impinger at 475 cc/min.

The precision of colorimetric analysis of hydrazine vapor mixtures was about $\pm 6\%$ as determined by repeated analysis of a single gaseous mixture, but the precision of the analysis of the standard aqueous hydrazine solutions was about $\pm 1\%$ indicating that the greatest source of error is in the collection of the vapors.

The lowest detectable concentrations of hydrazines in the aqueous state for procedures employed are 0.5 ppm, 0.05 ppm and 0.2 ppm for MMH, N_2H_4 and UDMH respectively. Since the concentration of aqueous hydrazines depends upon the volume of vapor mixture collected as well as the concentration of the hydrazine vapor, extremely low concentrations of hydrazine can be detected, as long as enough vapor is collected. To realize the stated accuracy, the volume of vapor which needs to be collected are given in TABLE XIV at the various levels of concentration.

IV. CONCLUSIONS AND RECOMMENDATIONS

Fixed installation 7000 Series and a portable 6000 Series hypergolic vapor detection instrumentation has been developed, designed, fabricated, and tested. Accessory hardware and supporting technology has been developed. These instruments are capable of reliable measurement of H, MMH, UDMH, and NO_2 and meet this program's required design goals.

The success of this type of instrumentation gives impetus to the future development of more advanced electrochemical instrumentation. The present technology, for the first time introduces a cost-effective and reliable method for field measurement of hypergolic vapors. Yet these instruments will not provide for all the needs of future hydrazine instrumentation

TABLE XIV
VOLUME VAPOR NECESSARY FOR SPECIFIED ACCURACY USING COLORIMETRIC ANALYSIS

	MMH	N ₂ H ₄	UDMH
0.1 ppm	106 Liters	19.1 Liters	33.4 Liters
1 ppm	10.6 Liters	1.91 Liters	3.34 Liters
10 ppm	1.06 Liters	0.19 Liters	0.33 Liters

and while they are state-of-the-art instruments, they do not reveal ultimate capabilities for this electrochemical detection system.

Present limitations of the sensing technique are detection specificity and sensor lifetime. These characteristics can be improved by further sensor developments along with improvements in accuracy, environmental stability, sensitivity, and attitude sensitivity. Future applications of electrochemical sensing technology can be made in the development of analytical instrumentation, dosimeters, and safety monitors for hypergolic vapors.

REFERENCES

- 1) J.R. Stetter, "Study for Hypergolic Vapor Sensor Development", Final Report NASA Contract NAS 10-8982, April 8, 1977.
- 2) H.G. Oswin and K.F. Blurton, U.S. Patent 3,776,832.
- 3) H.G. Oswin and K.F. Blurton, U.S. Patent 3,824,167.
- 4) For example see: "NIOSH Analytical Methods for Set Q", Sept. 1976, Contract CDC-99-74-45; ASTM Designation: D-1385-67, "Standard Method of Test for Hydrazine in Industrial Water"; H. McKennis Jr. and A.S. Yard, Anal. Chem., 12, 1960 (1954); Personal Communications of the Author with: Dr. Alex Teass, NIOSH, "Hydrazine Compounds in Air (Analysis of)" 2/24/77; Dr. J.J. DeCorpo and Dr. R.A. Saunders, Naval Research Laboratory, Washington, D.C. 9/76; Dr. L.J. Luskus, USAF School of Aerospace Medicine, Brooks AFB, Texas 78235, 9/24/76.

APPENDIX I

OPERATION OF THE HYDRAZINES DILUTION APPARATUS

The Hydrazine Dilution Apparatus is used to make hydrazines vapor mixtures of < 1 ppm to > 100 ppm in a continuous manner. The dilution apparatus is shown in FIGURE I-A-1, which is contained in a large fume hood, since the hydrazines are of a toxic and dangerous nature. Also, any bottles or vials of neat hydrazines are kept in the hood.

The apparatus operates by supplying a uniform low flow of liquid Hydrazine, MMH, or UDMH contained in a 10 µl Hamilton syringe with a Sage Model 355 syringe pump through a septum sealed port into a custom fabricated glass mixing apparatus through which a diluent gas flows. 99.9998% N₂ was most frequently used as a diluent since hydrazines vapors were found to be more stable in N₂ than air. A controlled flow of the diluent gas passes through a pre-conditioning chamber, which may be used to warm the gas stream when relatively high concentrations (> 50 ppm) of Hydrazines are desired. It then passes the syringe needle, picking up the vapor and into a 1 liter bulb which mixes the vapor and diluent gas. The vapor mixture then may be divided by two teflon glass valves and the sampling stream passes a 603 Matheson flowmeter. The vapor mixtures may either be collected in Teflon bags for remote sampling or be used directly from the sample exit stream.

To set up the dilution system, the diluent gas source at 40 PSI (in the case of N₂, a gas tank) is connected to a manifold which supplies the diluent to the glass mixing apparatus. The diluent is adjusted to the desired sample flow (using the sample flowmeter with the vent valve closed) by using the appropriate valve on the manifold. A 10 µl syringe is filled with neat MMH, Hydrazine or UDMH from a Teflon valve cap vial containing the proper liquid, moving the plunger up and down several times to rinse and remove bubbles from the syringe. The syringe is injected into the septum port in the glass mixing apparatus, and placed on the syringe pump and secured with the clamp. The syringe pump carriage is placed on the pump and the syringe pump is

put on a high speed until the carriage is just pushing the syringe plunger. The pump is then adjusted to some lower delivery rate (for example settings 60% flow X $\frac{1}{1000}$). After allowing 15 minutes for the system to reach steady state, the vapor mixture is ready to be sampled.

The theoretical concentration of the vapor can be found by knowing the delivery rate of the liquid and the flowrate of the diluent. The equation giving the ppm vapor concentration by volume is:

$$[\text{MMH, H, or UDMH}] = \frac{AD \times 24450 \frac{\text{ml}}{\text{mole}} \times 10^6 \text{ ppm}}{MF}$$

where: A = the delivery rate Hydrazines liquid ($\frac{\text{ml}}{\text{min}}$).

D = the density of the liquid (g/ml).

M = the molecular weight of the liquid ($\frac{\text{g}}{\text{mole}}$).

F = the flowrate of the diluent (ml/min).

Since the syringe pump delivers 0.024 ml/min for a 10 μl syringe at pump settings 100% Flow X 1, A is given by:

$$A = 0.024 \text{ ml/min} \times \frac{BC}{100\%} \quad (2)$$

where B = % Flow

$$C = \text{X1, } \times \frac{1}{10}, \times \frac{1}{100} \text{ or } \times \frac{1}{1000}.$$

Substituting equation (2) into (1) gives:

$$[\text{MMH, H, or UDMH}] = \frac{0.024 \text{ ml/min} \times BCD \times 24450 \text{ ml/mole} \times 10^6 \text{ ppm}}{M F 100\%} \quad (3)$$

(For example MMH at pump settings 60% X $\frac{1}{1000}$ and diluent flow of 700 ml/min yields

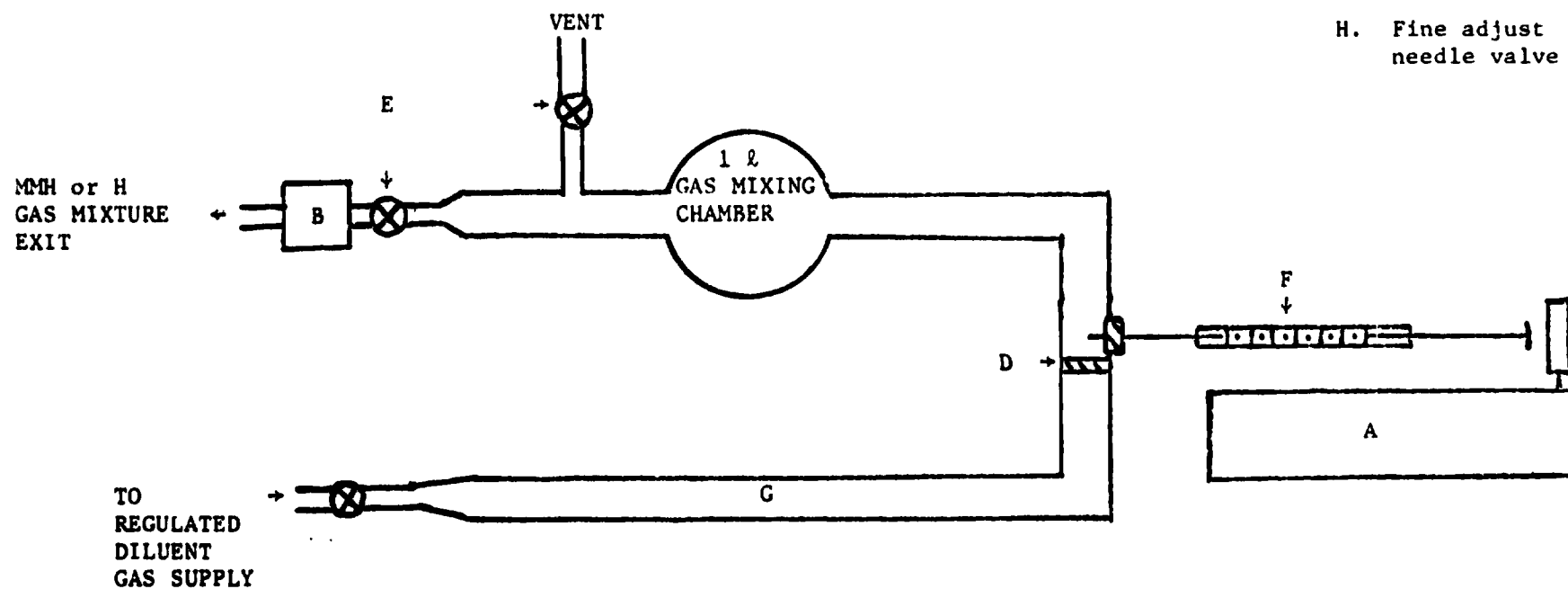
$$[\text{MMH}] = \frac{0.024 \text{ ml/min} \times 0.866 \text{ g/ml} \times 60\% \times \frac{1}{1000} \times 24,450 \text{ ml/mole} \times 10^6 \text{ ppm}}{\times 46 \text{ g/mole} \times 100\% \times 700 \text{ ml/min}} = 9.4 \text{ ppm.}$$

Bag samples are collected by disconnecting the sample stream from the flowmeter and connecting a Teflon bag to the sample stream. The bag is left on until it is 95% full. The bag is then removed and its valve is closed. The sample stream is replaced on the flowmeter. The bag may then be calibrated colorimetrically or electrochemically and used for remote sampling.

For direct sampling the sample stream is connected to a 500 ml plastic bottle with a sample exit and a vent. A portion of the sample stream is then drawn for testing.

LEGEND

- | | |
|--------------------------------|-------------------------------------|
| A. Sage Model 355 Syringe Pump | E. Flow control Teflon/glass valves |
| B. 0-2000 cc/min Flowmeter | F. Syringe |
| C. Septum Sealed Port | G. Diluent Pre-conditioning |
| D. Porous Glass Frit | H. Fine adjust needle valve |



APPENDIX II

ANALYTICAL PROCEDURES FOR H, MMH, AND UDMH ANALYSIS

- A. Determination of Gaseous Monomethylhydrazine.**
- B. Determination of Gaseous Hydrazine.**
- C. Determination of Gaseous Unsymmetrical Dimethylhydrazine.**

APPENDIX II-A

DETERMINATION OF GASEOUS MONOMETHYLHYDRAZINE

A. Preparation of PDMAB Dye Solution

- 1) MIX:
1.6 g. p-dimethylaminobenzaldehyde
15 ml concentrated HCl
200 ml Methanol
- 2) Store the dye solution in an amber bottle in a dark place.
Shelf life two weeks.

B. MMH Stock Solution, 100 ppm

- 1) Carefully weigh 0.156 g. of MMH. H_2SO_4 salt on an analytical balance.
- 2) Completely transfer the MMH . H_2SO_4 to a 500 ml volumetric flask containing about 100 ml 0.1 N H_2SO_4 . Shake the flask, dissolving the MMH. H_2SO_4 . Fill to the mark with 0.1 N H_2SO_4 .

C. Use of the Spectronic 20 Colorimeter

- 1) With the instrument off, ensure that the "blue" phototube, number CE-A59RX (gray internals), for wavelengths less than 650 nm is installed.
- 2) Turn the instrument on by rotating the Power - Zero control clockwise and allow the instrument to warm up at least 30 minutes before use.

D. Sampling

- 1) Pipet 25 ml of 0.1N H_2SO_4 into a midget impinger with a bubbler attachment.
- 2) Connect the inlet of the impinger to a female fitting to allow easy bag sampling. Connect the outlet to a flowmeter and the flowmeter to a valve and the valve to a pump with tygon tubing (See Figure III-A-1).
- 3) Turn the pump on and adjust the flowrate between 700 and 200 cc/min with the valve. NOTE the flowrate.
- 4) Calculate the time needed to collect the desired volume of MMH/ N_2 or MMH/Air by the equation:

$$\text{Collection time (Minutes)} = \frac{\text{F.R. (cc/min)}}{\text{Volume cc}}$$

Connect the bag sample or other source of MMH vapor to the impinger inlet and start stopwatch.

- 5) After collecting for the desired time, remove bag or other source of MMH, stop stopwatch and turn off pump.
- 6) Collect 106 liters at 0.1 ppm MMH, 10.6 liters at 1 ppm MMH, and 1.06 liters at 10 ppm MMH. This volume needs to be determined by trial and error for unknown vapor samples.

Analysis

- 1) Turn on the Spectronic 20 and allow it to warm up.
- 2) Prepare a blank by pipeting 5 ml of 0.1N H₂SO₄ to one of the test tube cells-supplied with the colorimeter.
- 3) Pipet 5 ml of the sample solution in the impinger to a colorimeter test tube.
- 4) Pipet 2 ml of the PDMAB dye solution to each of the test tubes.
- 5) Stopper the test tubes and allow to stand for 30 minutes.
- 6) After 30 minutes, read the %T as follows:
 - a) Set the Spectronic 20 wavelength dial at 457 nm and adjust the zero control so that the meter reads 0%T with the cell holder empty and the cover closed.
 - b) Ensure that there are no bubbles in the blank sample and wipe the outside of the cell clean with a tissue. Open the cell holder cover and insert the test tube cell, aligning the mark on the cell with the line on the holder.
 - c) Close the cover and adjust the LIGHT control until the meter reads 100%T.
 - d) Remove the blank and save for future use.
 - e) Ensure that the sample cell contains no bubbles and wipe the outside clean with a tissue. Insert the cell in the holder, aligning the mark on the cell with the mark on the holder.
 - f) Close the cover and read %T. NOTE the result.
 - g) Repeat, steps b,c,d,e, and f three times and take average %T value.
- 7) Remove sample from colorimeter. If additional samples have been prepared for measurement, repeat steps 6b through 6g for each sample.
- 8) Convert the average %T of the sample to A (absorbance) by the formula:
$$A = \log \left(\frac{100}{\%T} \right)$$
- 9) Obtain the MMH value from the calibration curve.

F. Calculation

The concentration of gaseous MMH in N₂ or air is found by the equation:

$$\text{ppm MMH} = A \frac{13.3}{A}$$

A = ppm MMH in the solution sample.

V = volume MMH/N₂ or MMH/Air collected in cc?

G. Calibration Curve

- 1) Prepare a 10 ppm MMH standard solution by pipeting 10 ml of the stock solution to a 100 ml volumetric flask and diluting to the mark with 0.1N H₂SO₄. Repeat for standard solutions of 8, 5, 2 and 1 ppm MMH by pipeting 8, 5, 2, and 1 ml respectively instead of 10 ml.
- 2) Follow steps E1 through E8 in the analysis using the standard solutions as samples. Plot A, absorbance, vs. ppm MMH on graph paper. Draw the best straight line through the points and extrapolate to 0 ppm.
- 3) A separate curve shall be prepared for each colorimeter. A new curve, shall be prepared if it is necessary to change the colorimeter lamp or phototube.
- 4) Standard samples should be run periodically (i.e., one with each days calibrations) to check the accuracy of the calibration curve.

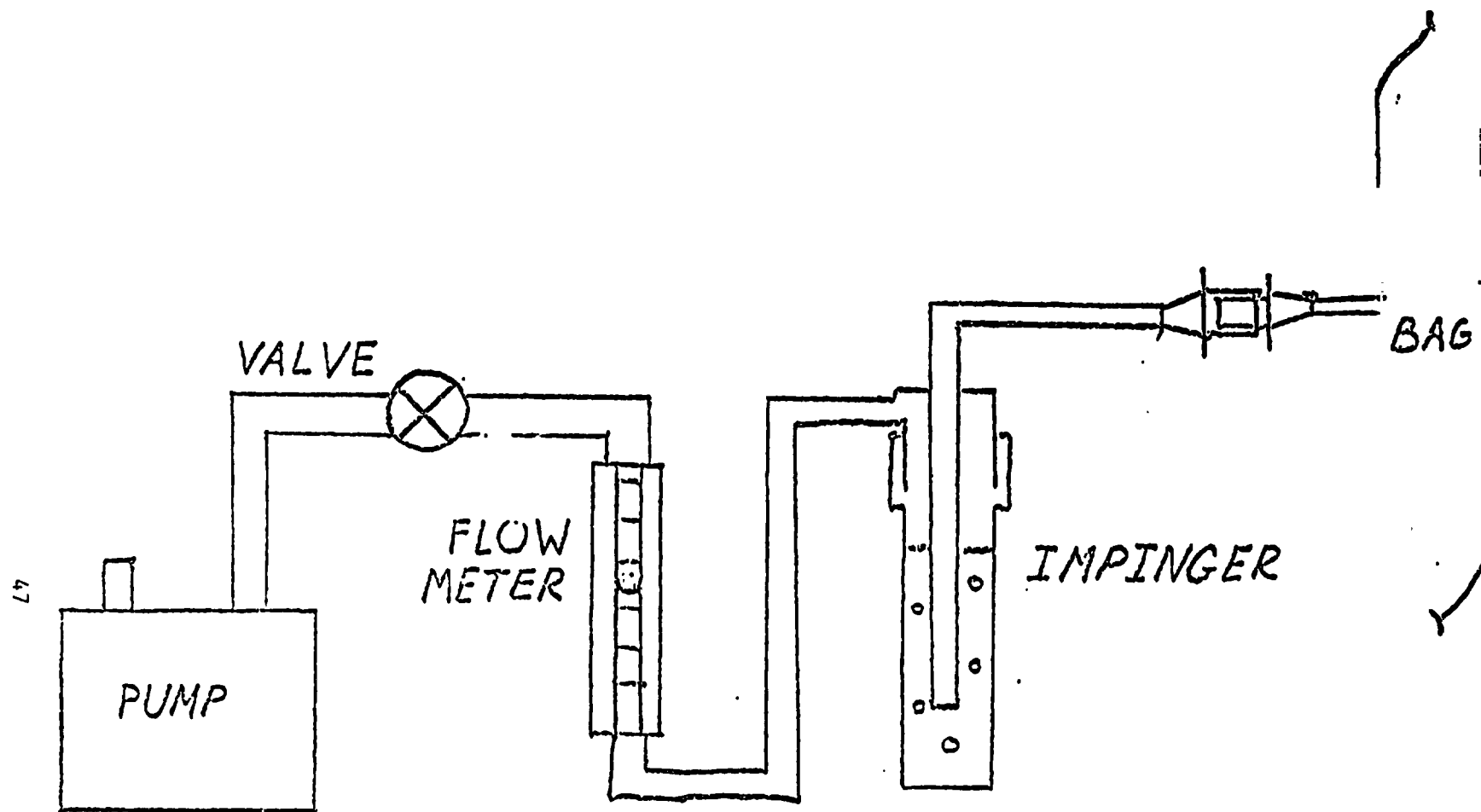


FIGURE II - A - 1

APPENDIX II - B

DETERMINATION OF GASEOUS HYDRAZINE

A. Preparation of PDMA B Dye Solution

- 1) Refer to Section A in the Determination of Monomethylhydrazine Appendix II-A.

B. N₂H₄ Stock Solution, 100 ppm

- 1) Carefully weigh 0.152 g. of N₂H₄·(HCl)₂ salt on an analytical balance.
- 2) Completely transfer the N₂H₄·(HCl)₂ to a 500 ml volumetric flask containing about 100 ml 0.1N HCl. Shake the flask, dissolving the N₂H₄·(HCl)₂. Fill to the mark with 0.1N HCl.

C. Use of the Spectronic 20 Colorimeter

- 1) Refer to Section C in the Determination of Monomethylhydrazine; Appendix II-A.

D. Sampling

- 1) Pipet 25 ml of 0.1N HCl into a midjet impinger with a bubbler attachment.
- 2) Refer to Sections D 2-5 in the Determination of Monomethylhydrazine, Appendix II-A.
- 3) As a guide, collect 19 liters at 0.1 ppm H, 1.9 liters at 1 ppm H, and 0.2 liters at 10 ppm H.

E. Analysis

- 1) Turn on the Spectronic 20 and allow it to warm up.
- 2) Prepare a blank by pipeting 25 ml of 0.1N HCl into a small vial.
- 3) Transfer the entire impinger sample to a small vial.
- 4) Pipet 1.25 ml of the PDMA B dye solution to each of the vials.
- 5) Cap the vials and allow to stand for 20 minutes.
- 6) After 20 minutes, read the %T as follows:
 - a) Set the Spectronic 20 wavelength dial at 457 nm and adjust the zero control so that the meter reads 0%T with the cell holder empty and the cover closed.
 - b) Rinse a test tube cell twice with the blank and fill halfway with the blank. Wipe the outside of the cell clean with a tissue. Open the cell holder cover and insert the test tube cell, aligning the mark on the cell with the line on the holder.

- c) Close the cover and adjust the LIGHT control until the meter reads 100%T.
- d) Remove the blank and save for future use.
- e) Rinse a cell twice with the sample and fill halfway with the sample. Wipe the outside clean with tissue. Insert the cell in the holder, aligning the mark on the cell with the mark on the holder.
- f) Close the cover and read %T. NOTE the result.
- g) Repeat, steps b,c,d,e, and f three times and take average %T value.
- 7) Remove sample from colorimeter. If additional samples have been prepared for measurement, repeat steps 6b through 6g for each sample.
- 8) Convert the average %T of the sample to A (absorbance) by the formula:

$$A = \log \left(\frac{100}{\%T} \right)$$

- 9) Obtain the N_2H_4 value from the calibration curve.

F. Calculation

The concentration of gaseous N_2H_4 in N_2 or air is found by the equation:

$$\text{ppm } N_2H_4 = A \frac{19.1}{V}$$

A = ppm N_2H_4 in the solution sample.

V = volume N_2H_4/N_2 or N_2H_4/Air collected in cc?

G. Calibration Curve

- 1) Prepare a 10 ppm N_2H_4 standard solution by pipeting 10 ml of the stock solution to a 100 ml volumetric flask and diluting to the mark with 0.1N HCl. Repeat for standard solutions of 8,5,2, and 1 ppm N_2H_4 by pipeting 8,5,2, and 1 ml respectively instead of 10 ml.
- 2) Follow steps E1 through E8 in the analysis using the standard solutions as samples. Plot A, absorbance, vs. ppm N_2H_4 on graph paper. Draw the best straight line through the points and extra polate to 0 ppm.
- 3) A separate cover shall be prepared for each colorimeter. A new curve, shall be prepared if it is necessary to change the colorimeter lamp or phototube.
- 4) Check calibration often by analyzing a standard sample.

APPENDIX II - C

DETERMINATION OF GASEOUS UNSYMMETRICAL DIMETHYLHYDRAZINE

A. Preparation of Buffer Solution

- 1) MIX:
9.6 g Citric Acid
15.7 g Na_2HPO_4
2 liters distilled water.
- 2) Adjust the pH to 5.4 (with a pH meter)? with citric acid?

B. UDMH Stock Solution

- 1) Fill a 500 ml volumetric flask with buffer solution to the line.
- 2) Transfer (63 x (purity of UDMH)) μl of neat UDMH with a 100 μl syringe to the flask. Shake the flask.

C. Use of the Spectronic 20 Colorimeter

- 1) Refer to Section C in the Determination of Monomethylhydrazine Appendix II-A.

D. Sampling

- 1) Pipet 25 ml of buffer solution into a midget impinger with a bubbler attachment.
- 2) Refer to Sections D 2-5 in the Determination of Monomethylhydrazine, Appendix II-A, however the flowrate through the impinger should be between 200 and 400 cc/min.
- 3) As a guide, collect 33 liters at 0.1 ppm UDMH, 33 liters at 1.0 ppm UDMH, and 0.33 liters at 10 ppm UDMH.

E. Analysis

- 1) Turn on the Spectronic 20 and allow it to warm up.
- 2) Prepare a 0.1% TPF solution by transferring 0.1 g of trisodiumpentacyanoaminoferate into 10 ml volumetric flask and filling to the mark with distilled water.
- 3) Prepare a blank by pipeting 7 ml of the buffer solution to one of the test tube cells supplied with the colorimeter.
- 4) Pipet 7 ml of the sample solution in the impinger to a colorimeter test tube.
- 5) Pipet 1 ml of the TPF solution to each of the test tubes.
- 6) Stop the test tubes and allow to stand for 20 minutes.
- 7) After 30 minutes, read the %T as follows:

- a) Set the Spectronic 20 wavelength dial at 500 nm and adjust the zero control so that the meter reads 0%T with the cell holder empty and the cover closed.
 - b) Ensure that there are no bubbles in the blank sample and wipe the outside of the cell clean with a tissue. Open the cell holder cover and insert the test tube cell, aligning the mark on the cell with the line on the holder.
 - c) Close the cover and adjust the LIGHT control until the meter reads 100%T.
 - d) Remove the blank and save for future use.
 - e) Ensure that the sample cell contains no bubbles and wipe the outside clean with a tissue. Insert the cell in the holder, aligning the mark on the cell with the mark on the holder.
 - f) Close the cover and read %T. NOTE the result.
 - g) Repeat, steps b,c,d,e, and f three times and take average %T value.
- 8) Remove sample from colorimeter. If additional samples have been prepared for measurement, repeat steps 6b through 6g for each sample.
 - 9) Convert the average %T of the sample to A (absorbance) by the formula:

$$A = \log \left(\frac{100}{\%T} \right)$$

- 10) Obtain the UDMH value from the calibration curve.
- 11) NOTE: UDMH impinger sample should be analyzed within an hour of collection.

F. Calculation

The concentration of gaseous UDMH in N₂ or air is found by the equation:

$$\text{ppm UDMH} = A \frac{9.55}{V}$$

A = ppm UDMH in the solution sample.

V = volume UDMH/N₂ or UDMH/Air collected in cc?

Calibration Curve

- 1) Prepare a 10 ppm standard solution by pipeting 10 ml of the stock solution to a 100 ml volumetric flask and diluting to the mark with 0.1N H_2SO_4 . Repeat for standard solutions of 8, 5, 2 and 1 ppm MMH by pipeting 8, 5, 2, and 1 ml respectively instead of 10 ml.
- 2) Follow steps E1 through E8 in the analysis using the standard solutions as samples. Plot A, absorbance, vs. ppm MMH on graph paper. Draw a curve through the points and extrapolate to 0 ppm.
- 3) A separate curve shall be prepared for each colorimeter. A new curve, should be prepared if it is necessary to change the colorimeter lamp or phototube.

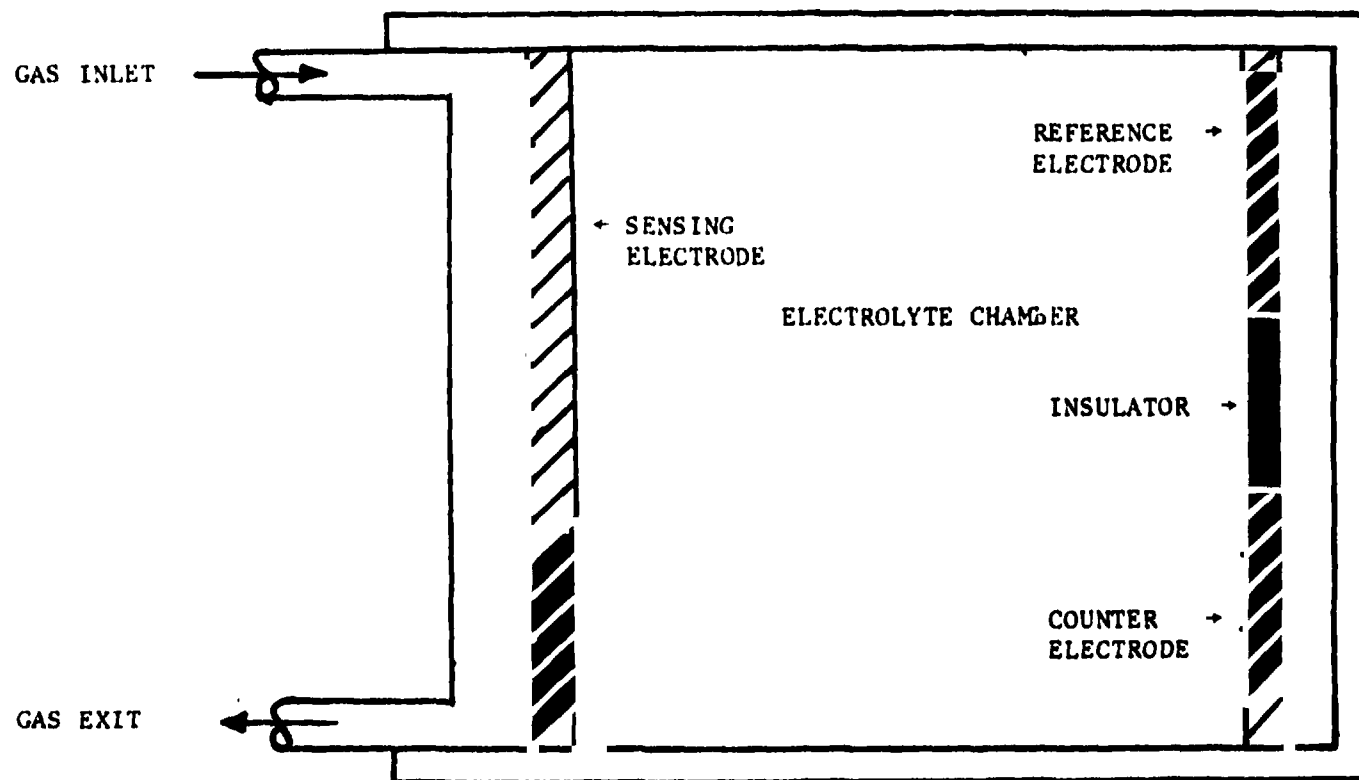


FIGURE 1 SCHEMATIC OF ELECTROCHEMICAL SENSOR

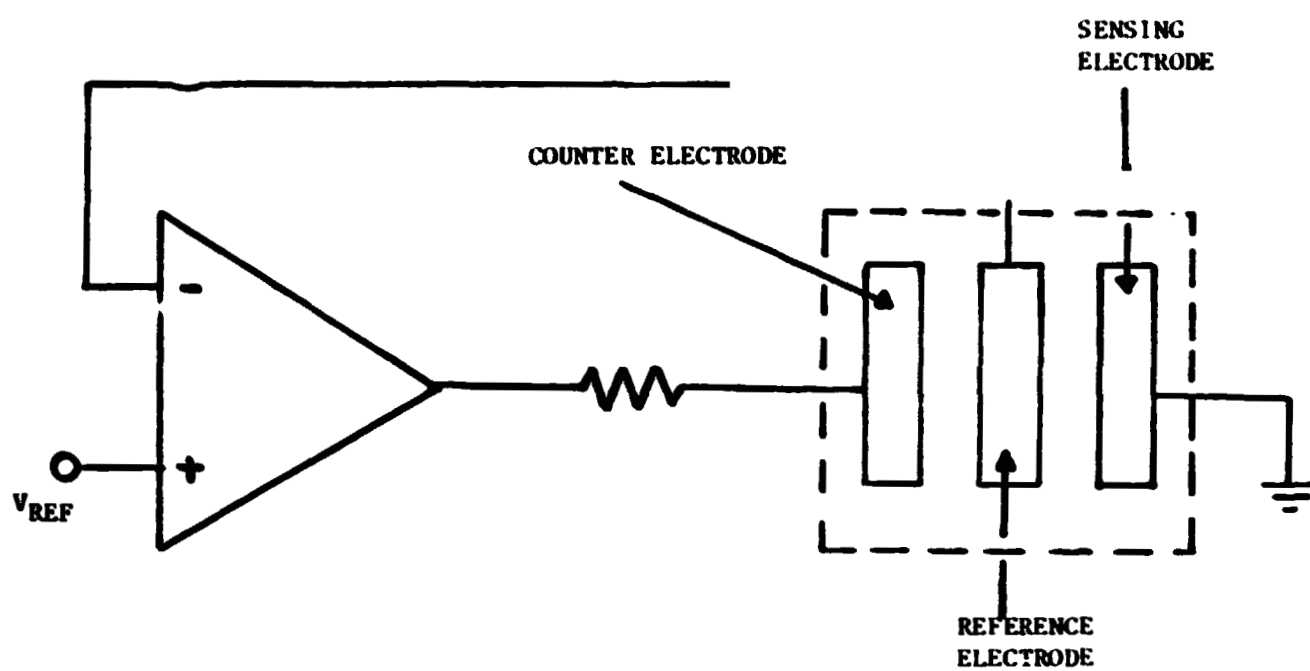


FIGURE 2 POTENTIOSTAT AND SENSOR ELECTRODES

FIGURE 3 MMH HIPSTER SENSOR RESPONSE TO 7.7 PPM MMH/N_2

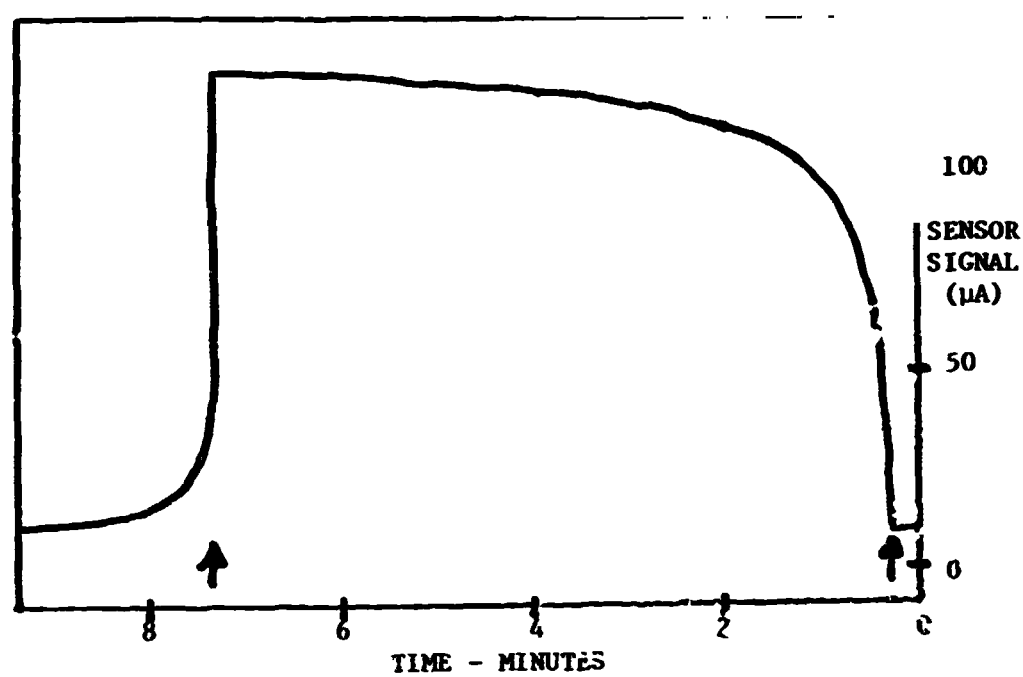
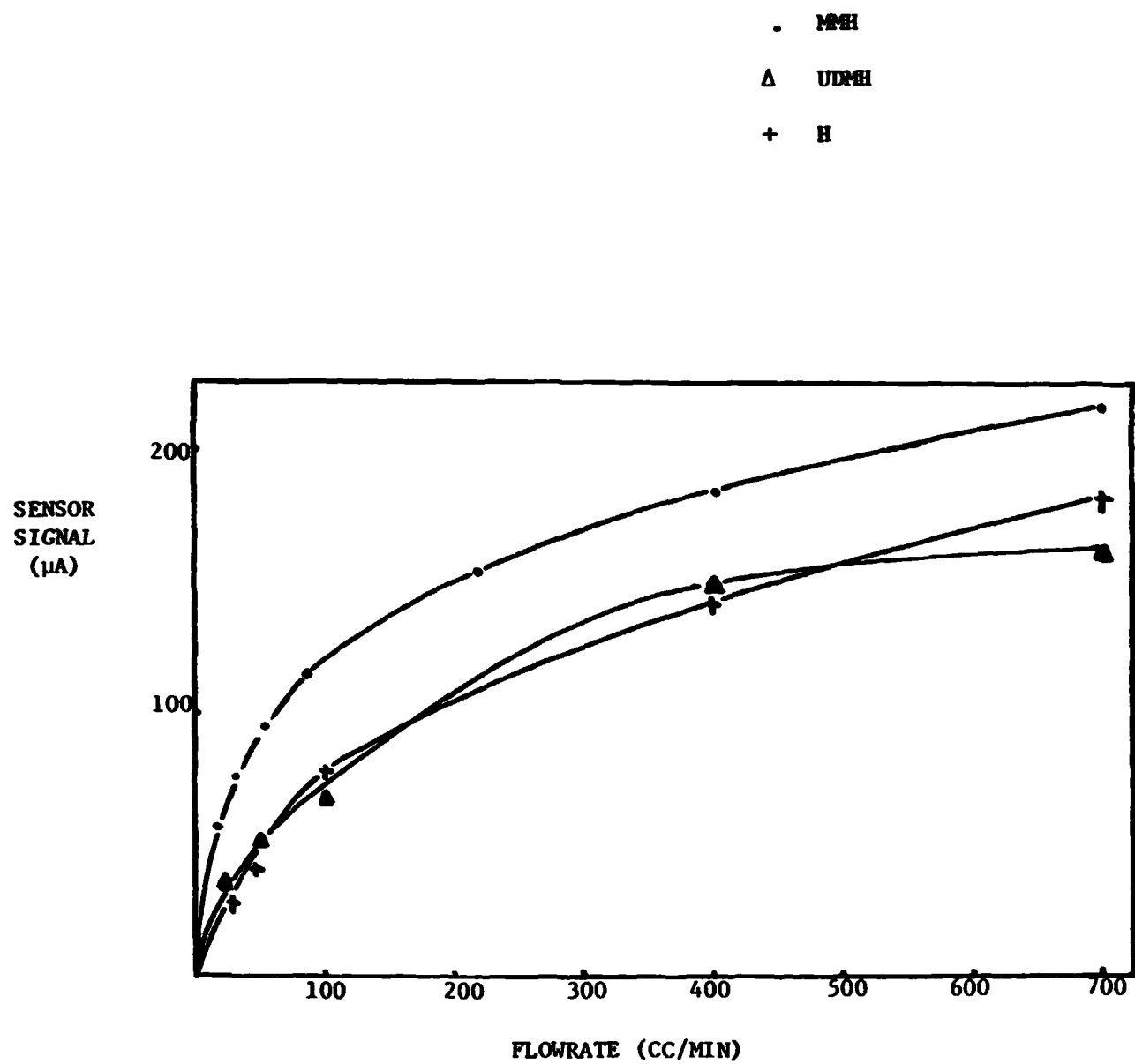


FIGURE 4 SENSOR SIGNAL VS. FLOWRATE



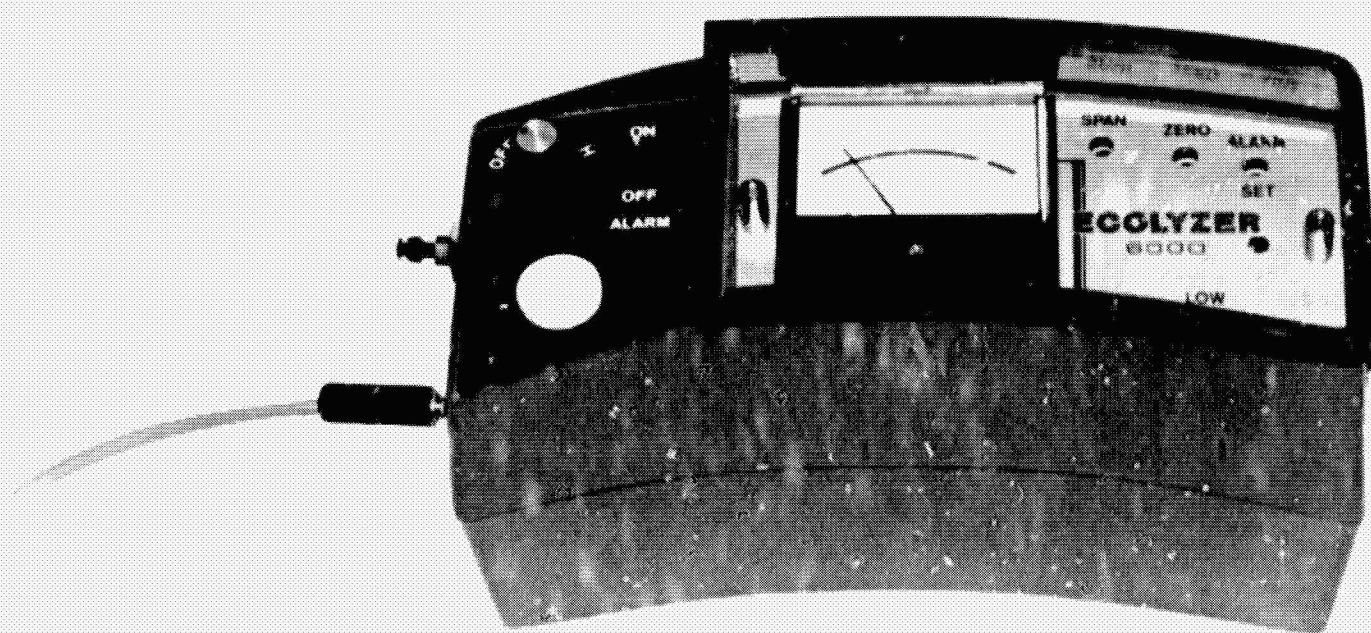


FIGURE 5
MMH HIPSTER

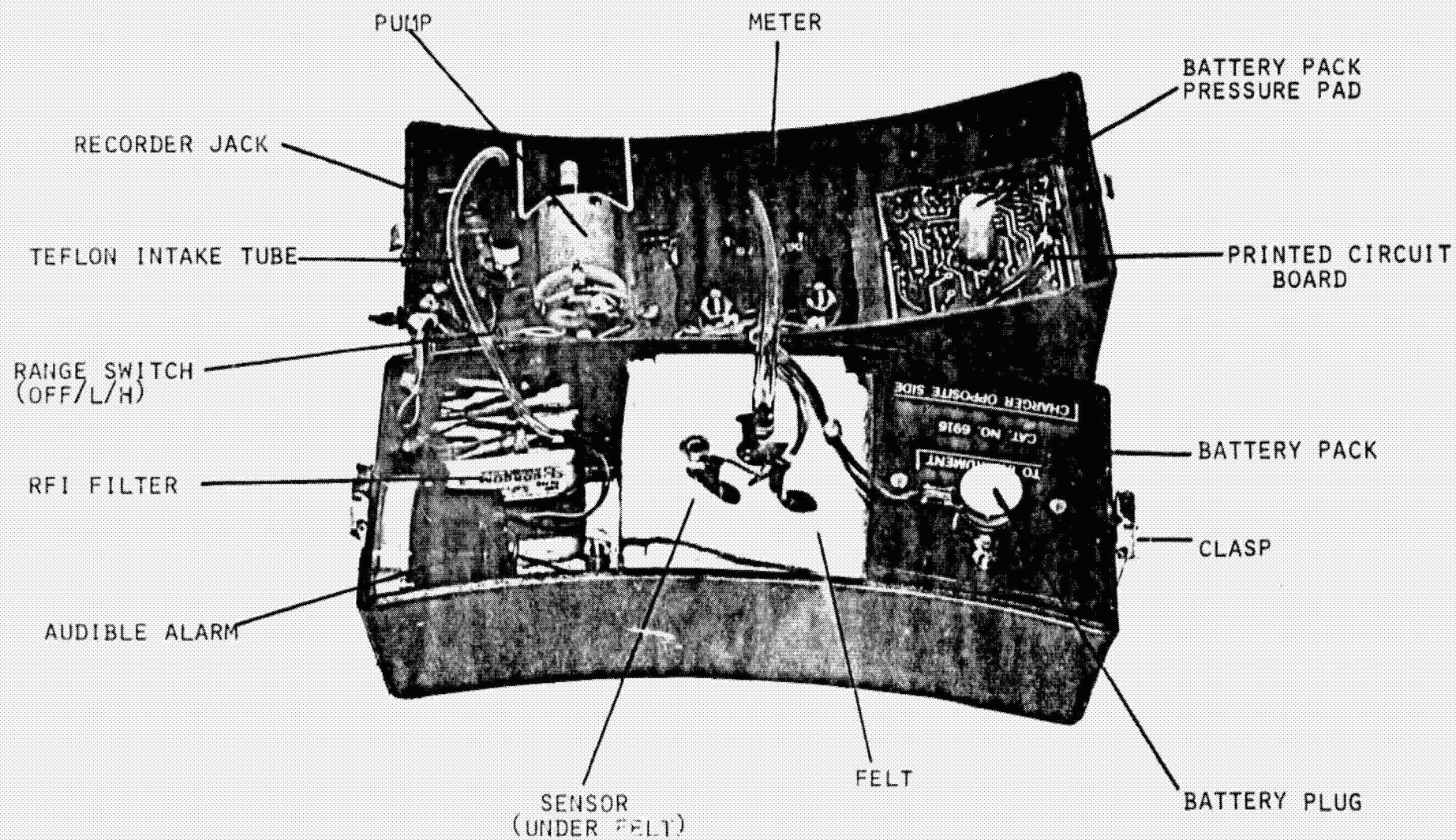


FIGURE 6 MMH HIPSTER INTERNAL

FIGURE 7 FLOW DIAGRAM OF THE MMH HIPSTER

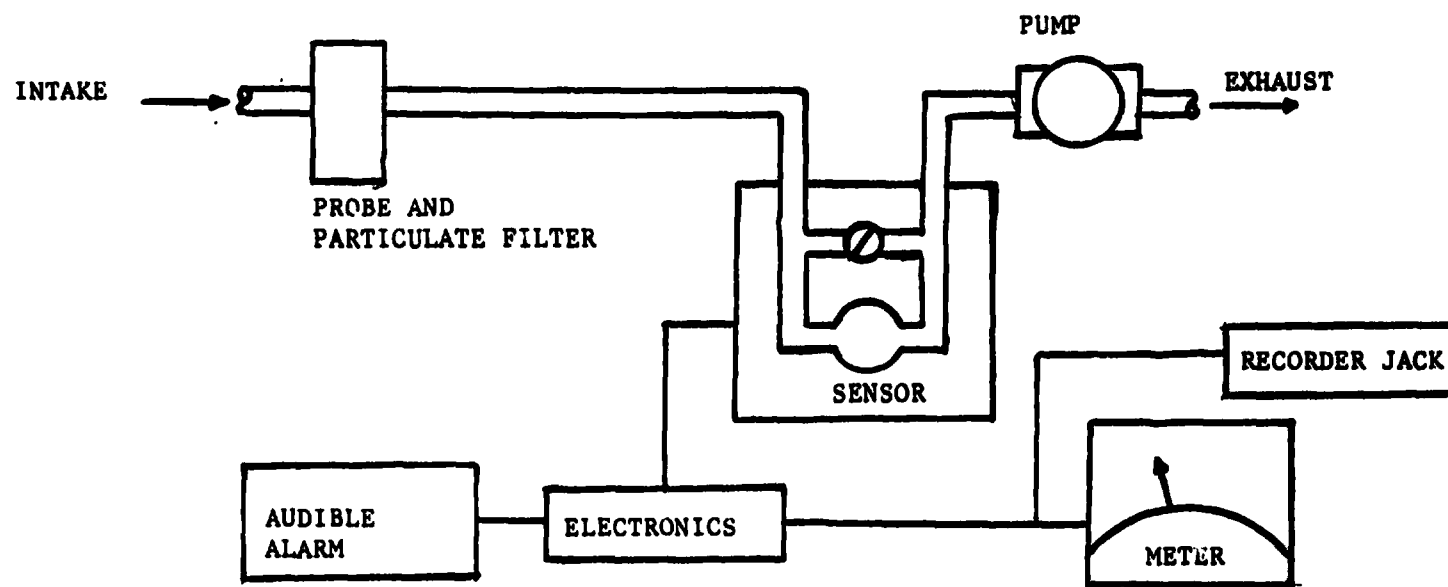
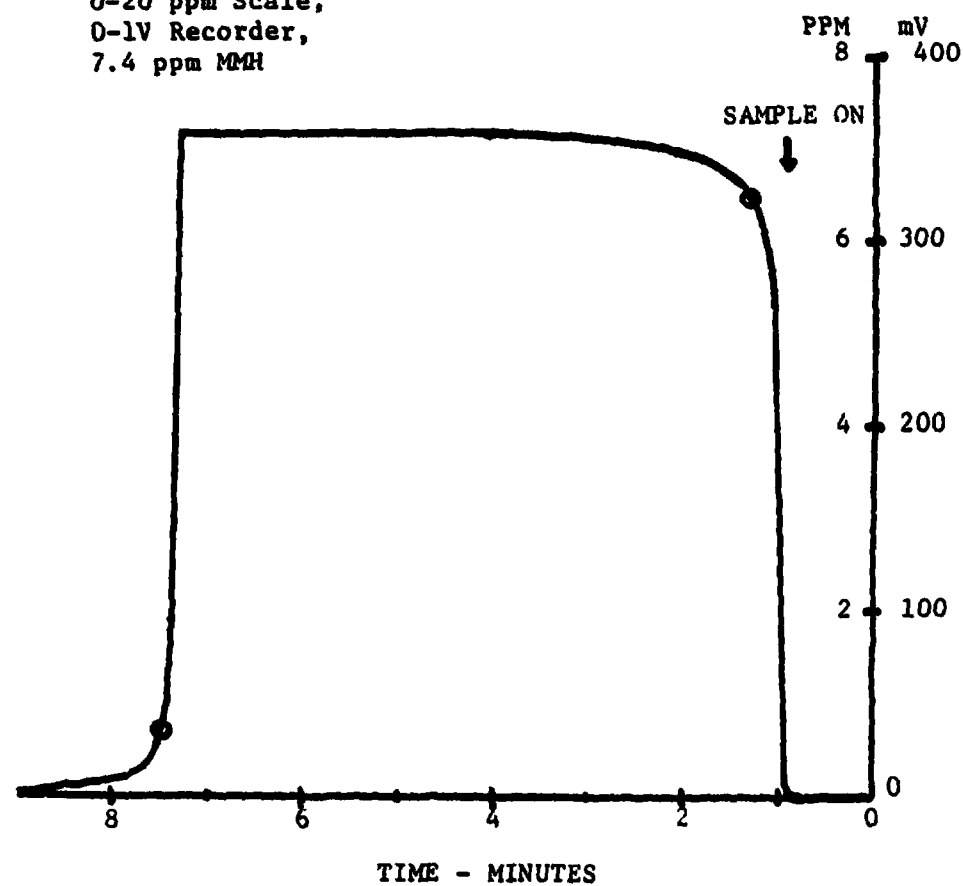


FIGURE 8

MMH RESPONSE FOR PROTOTYPE HIPSTER B001

ANALYSIS CONDITIONS:
0-20 ppm Scale,
0-1V Recorder,
7.4 ppm MMH



MMH RESPONSE FOR PROTOTYPE HIPSTER B002

ANALYSIS CONDITIONS:
0-20 ppm Scale,
0-1V Recorder,
7.4 ppm MMH

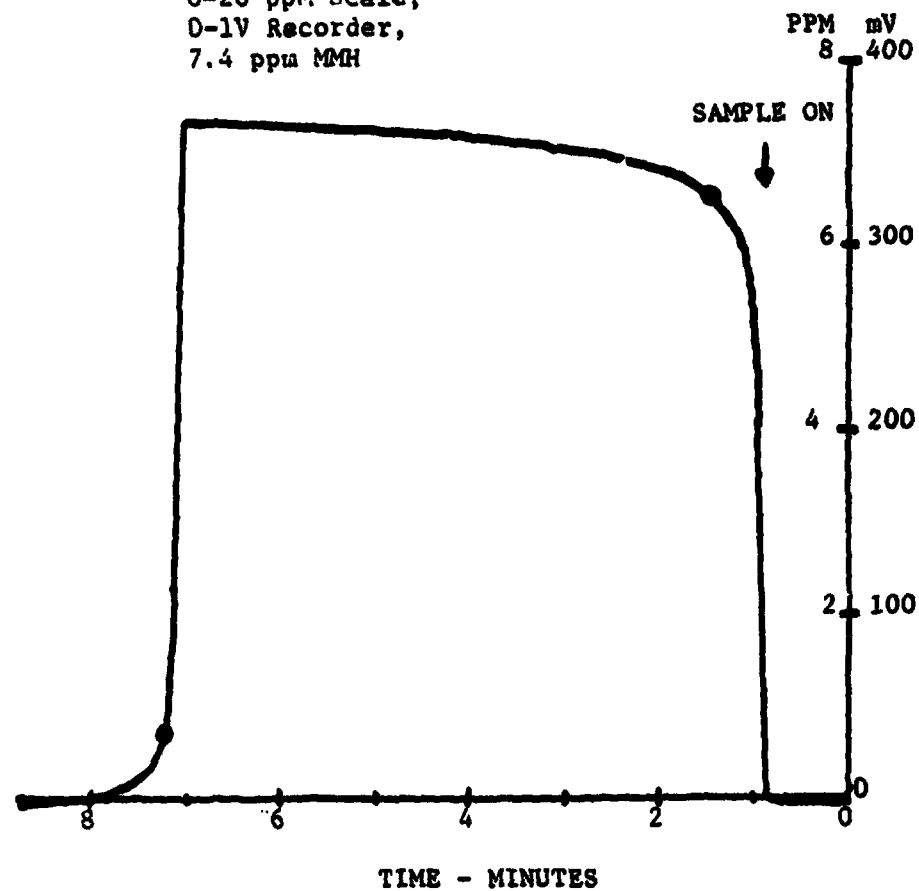


FIGURE 9 LINEARITY STUDY FOR MMH HIPSTER

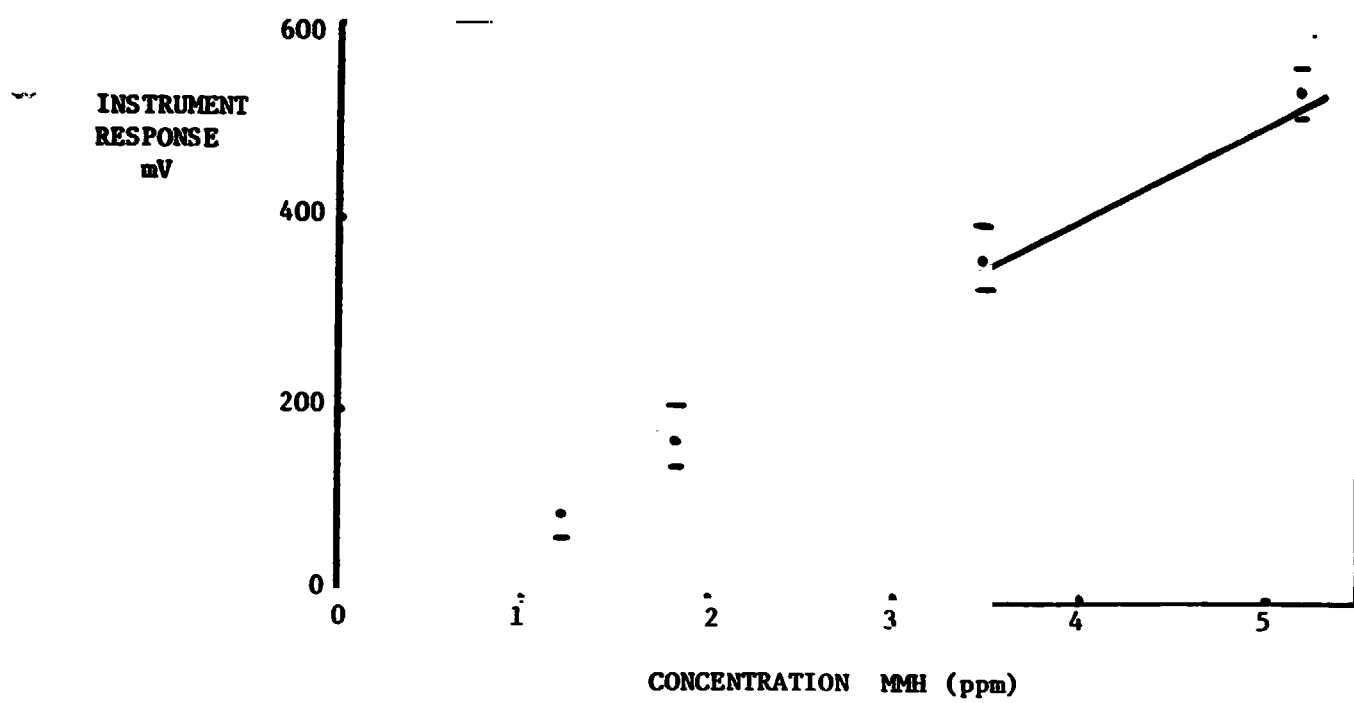
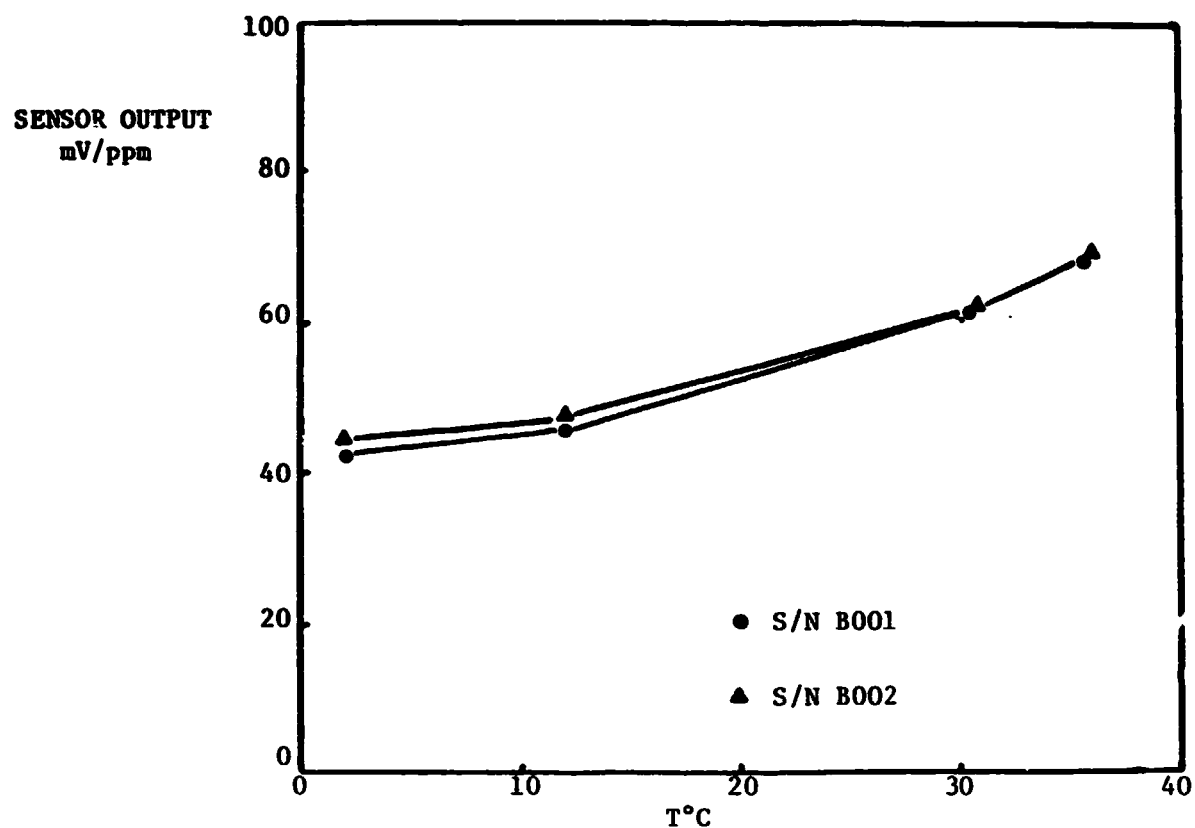


FIGURE 10 TEMPERATURE DEPENDENCE OF MODEL 6601 ECOLYZER

A. S.AN VS. TEMPERATURE



B. DYNAMIC ZERO VS. TEMPERATURE

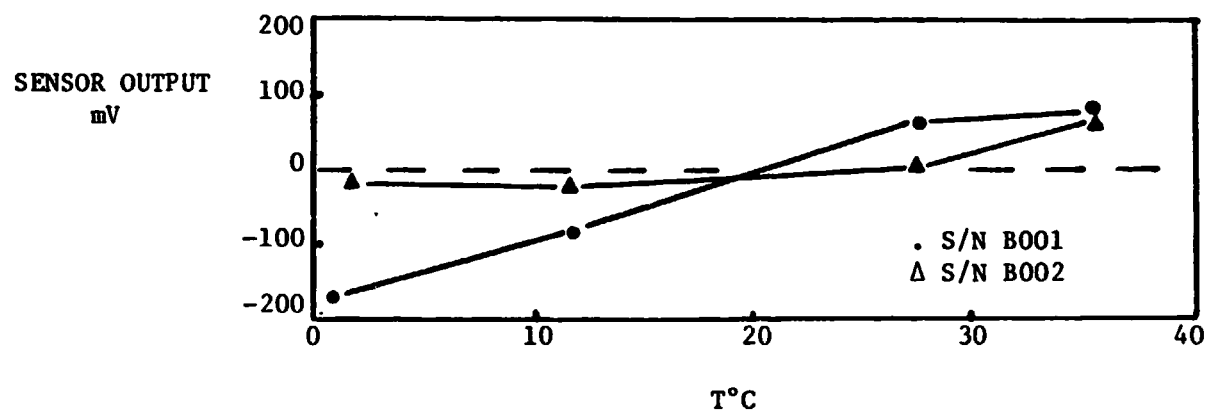
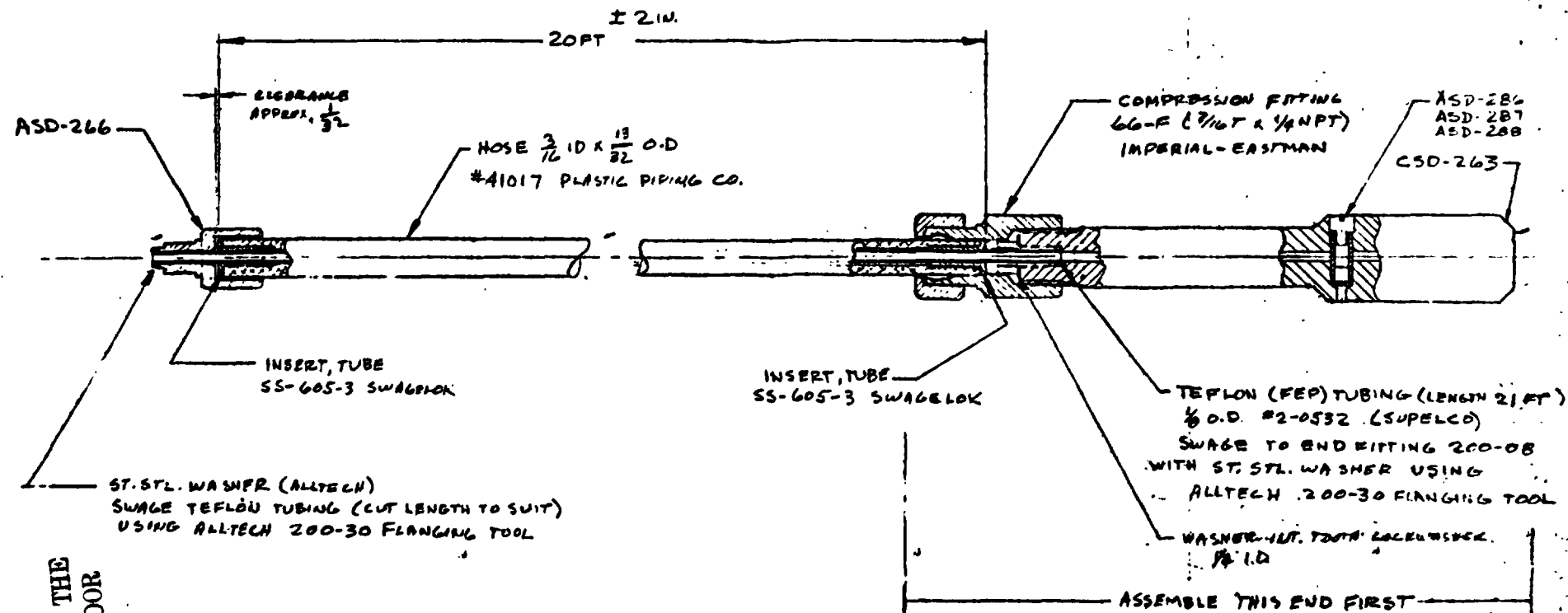


FIGURE 11

REVISION			
SYM	DESCRIPTION	CK	APP



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UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ON FRACTIONS & 1/16 DECIMALS & 1/32 ADDED & 1/64		ENERGETICS SCIENCE INC. ELMSFORD, N.Y.	
DESIGNER: [initials] ALL DIMENSIONS GIVEN FROM LEFT UNLESS OTHERWISE NOTED		PROBE ASSY HYDRAULIC HIPSTEE	
DATE: 1/5/75	BY: [initials]	CHKD: [initials]	REV: [initials]
FIG. NO. 051X-275			

FIGURE 12 INSTRUMENT RESPONSE TO 6.5 PPM MMH SAMPLE
THROUGH PROBE

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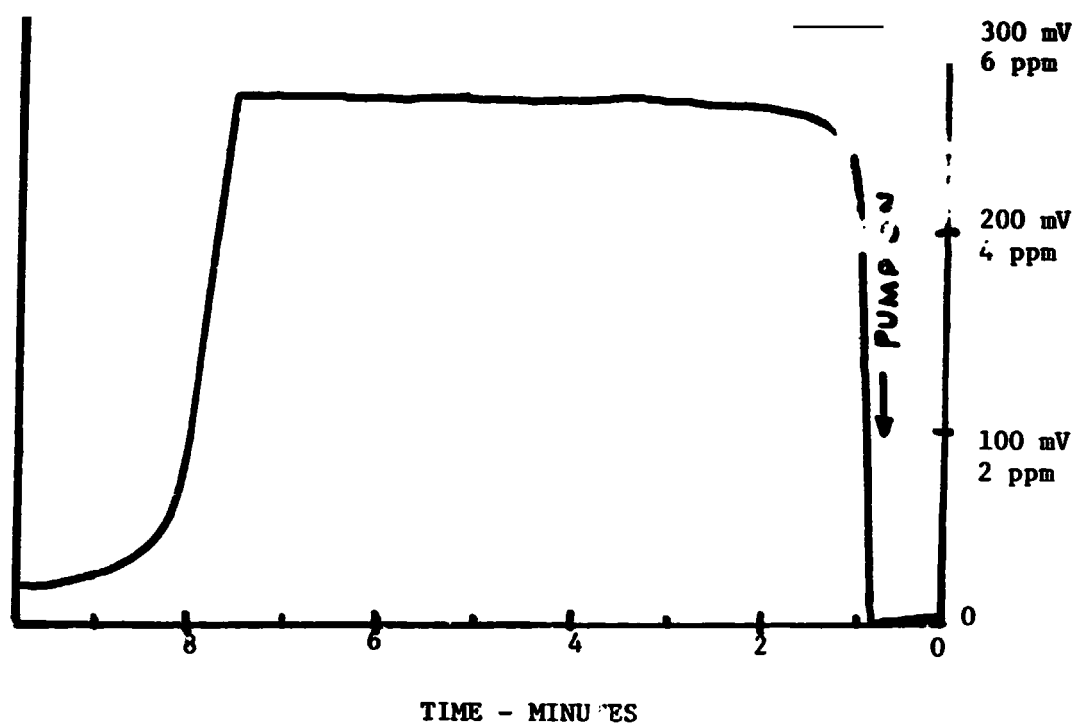


FIGURE 13 NO₂ SENSOR RESPONSE TO 9.59 PPM NO₂

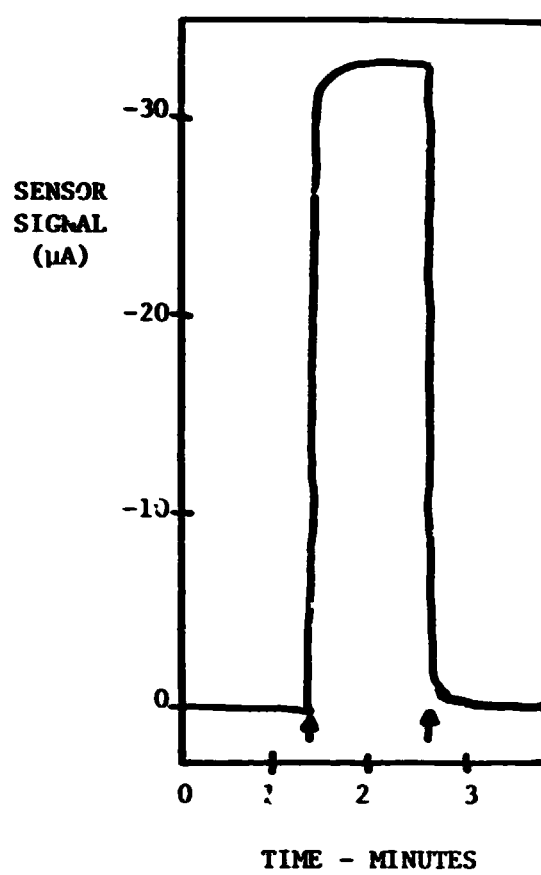
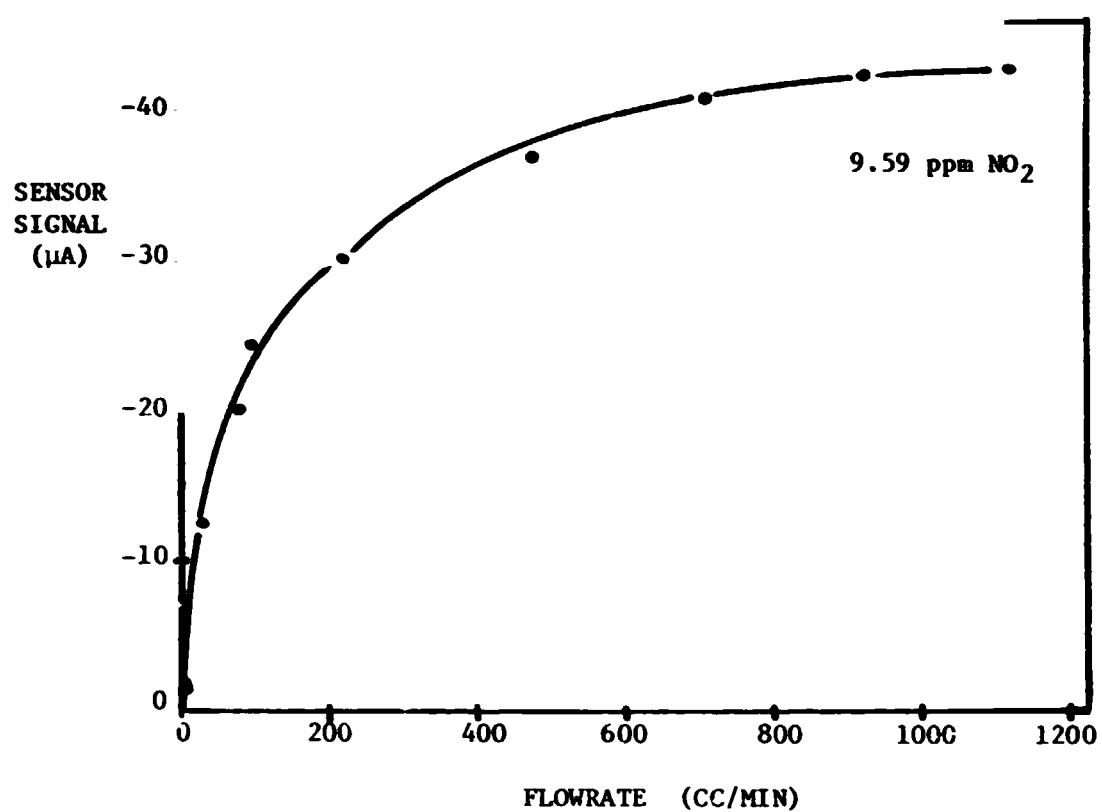


FIGURE 14 NO₂ HIPSTER SENSOR FLOWRATE DEPENDENCE



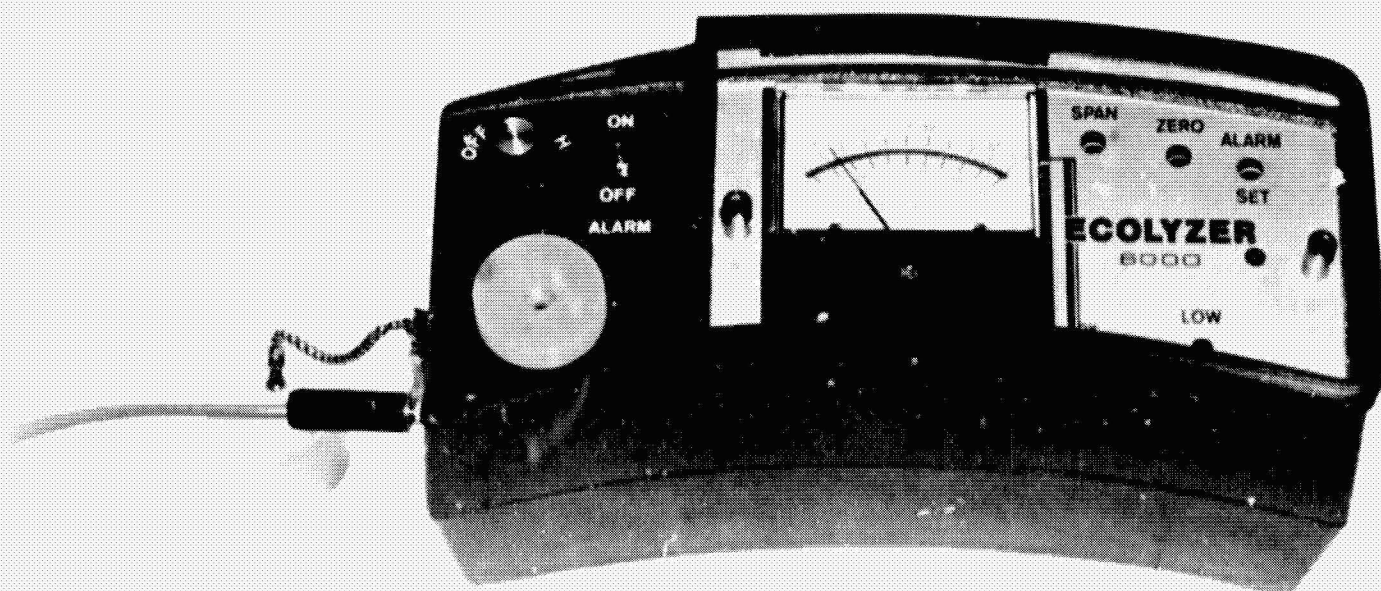


FIGURE 15

NO₂ HIPSTER

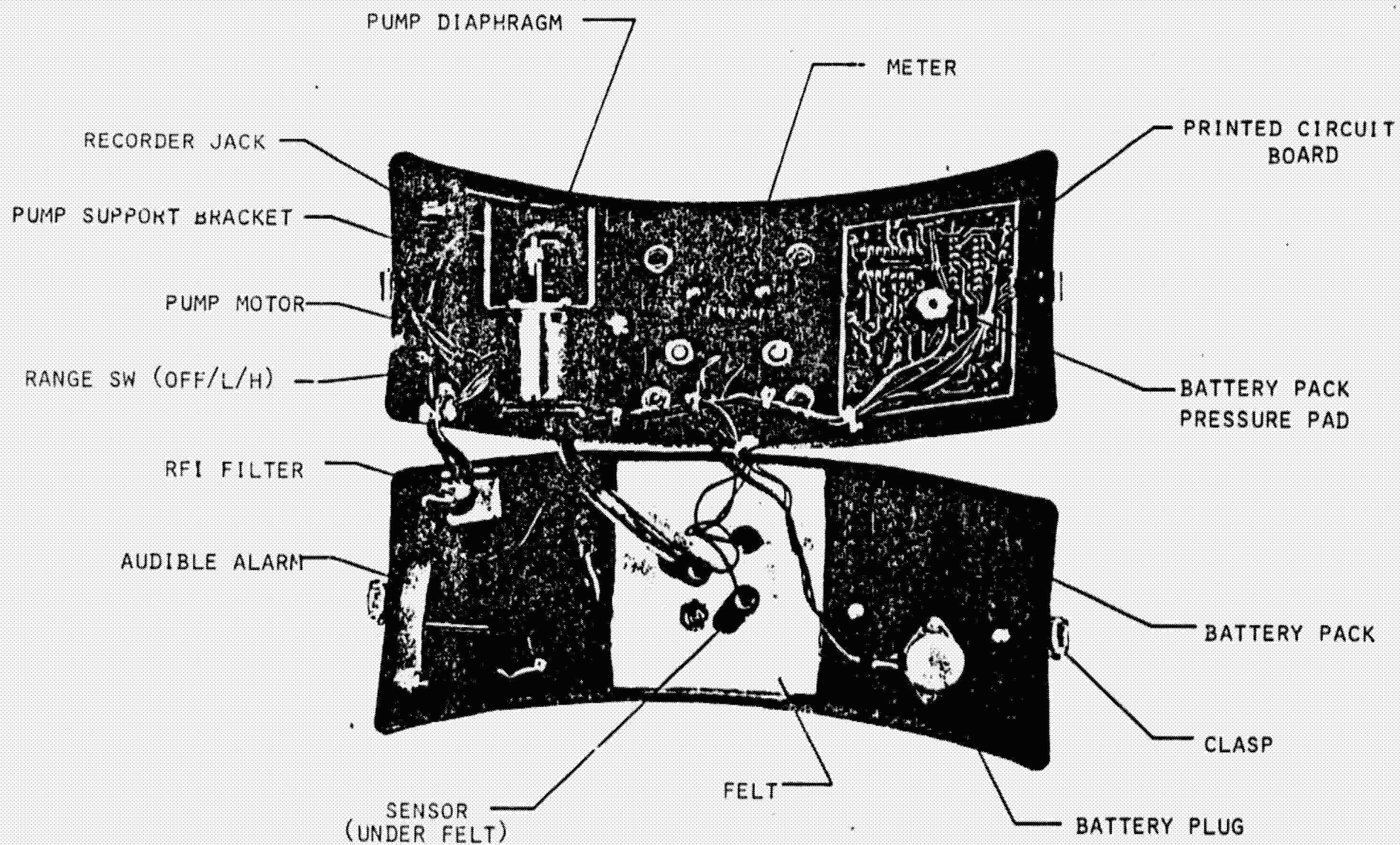


FIGURE 16
NO₂ HIPSTER INTERNAL

FIGURE 17 FLOW DIAGRAM OF THE NO₂ HIPSTER

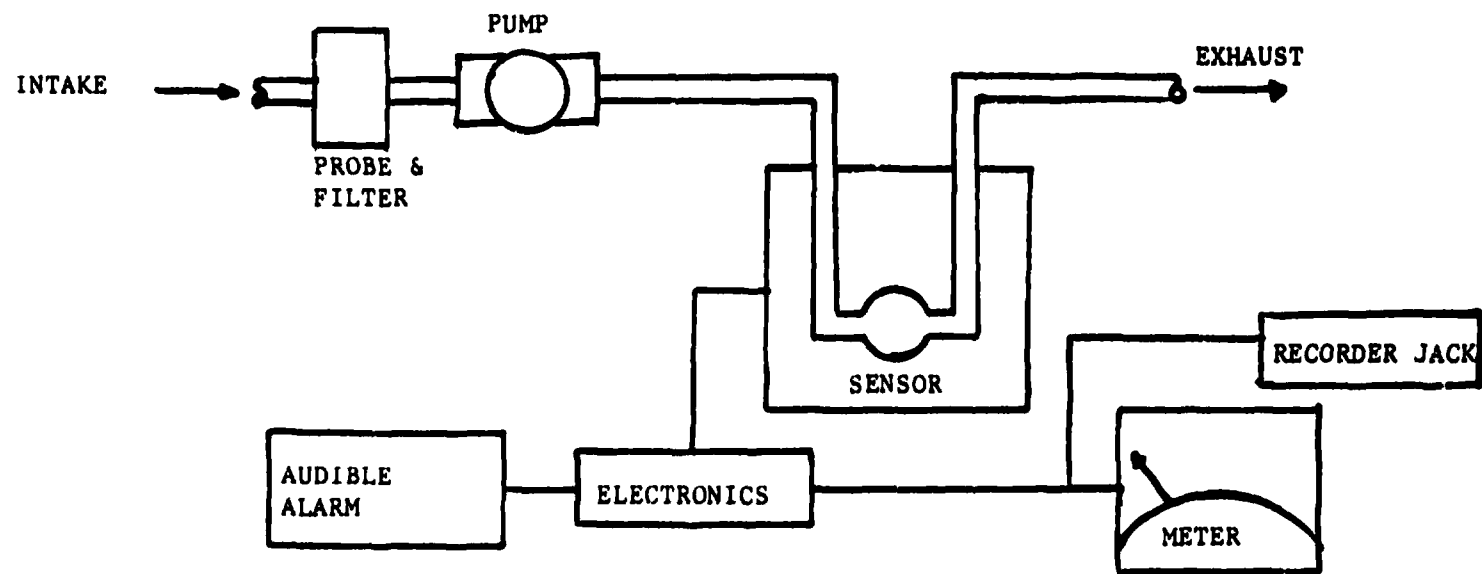
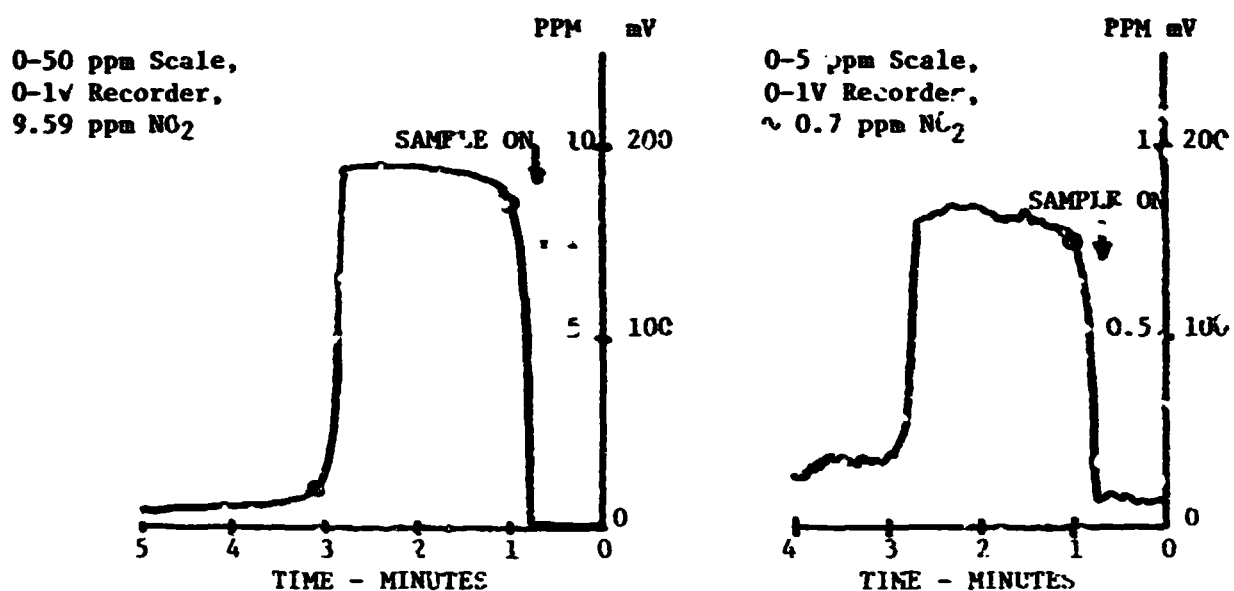


FIGURE 18 NO₂ RESPONSE OF PROTOTYPE HIPSTER A001



NO₂ RESPONSE OF PROTOTYPE HIPSTER A002

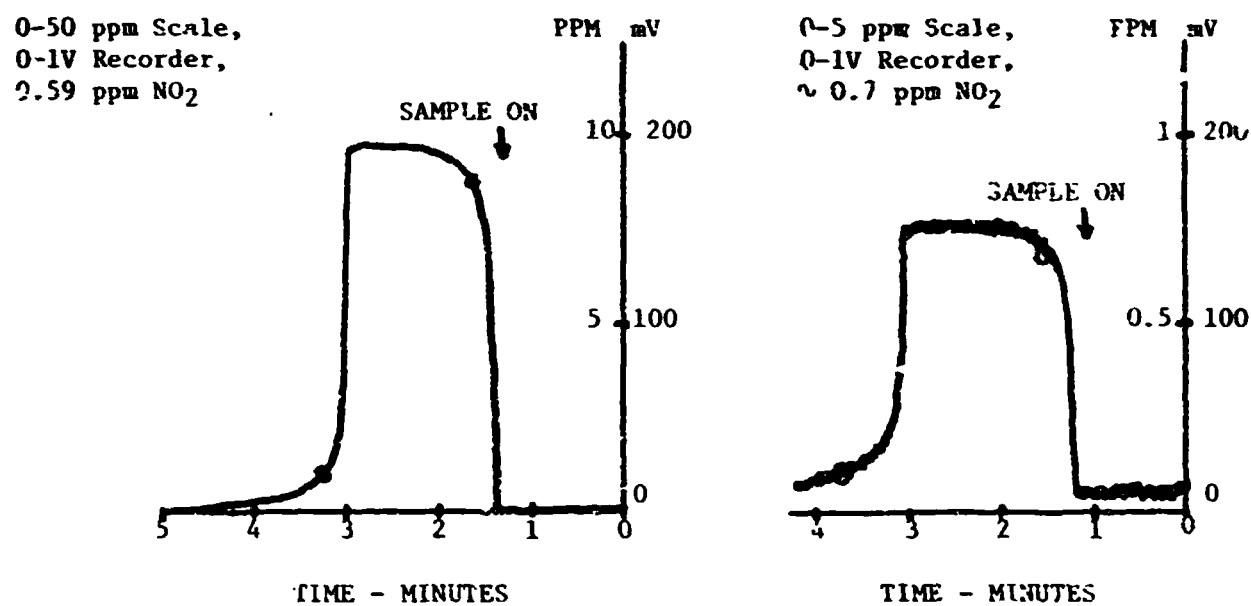


FIGURE 19 TEMPERATURE DEPENDENCE OF MODEL 6302 ECOLYZER

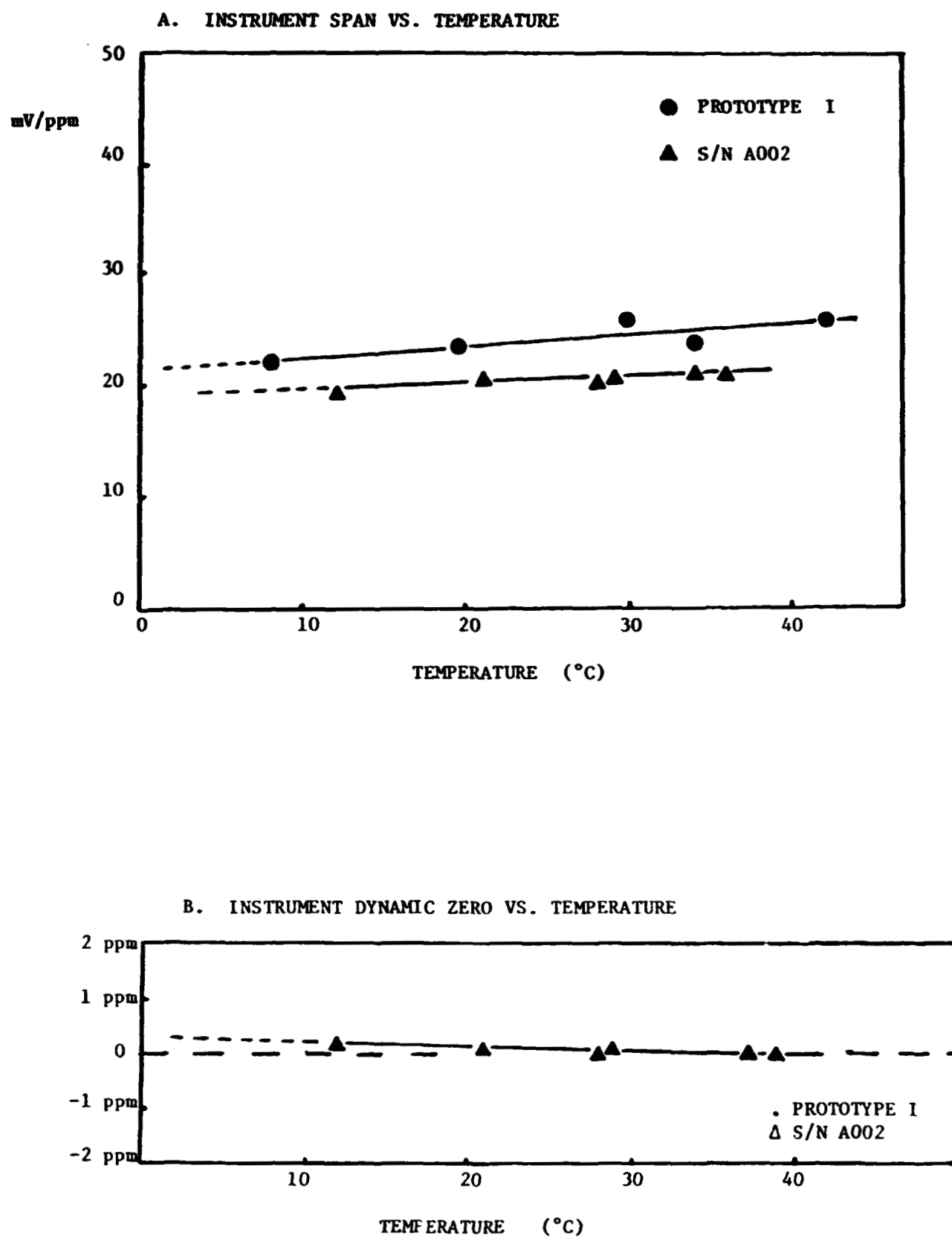


FIGURE 20 MODEL 6302 NO₂ ECOLYZER LINEARITY

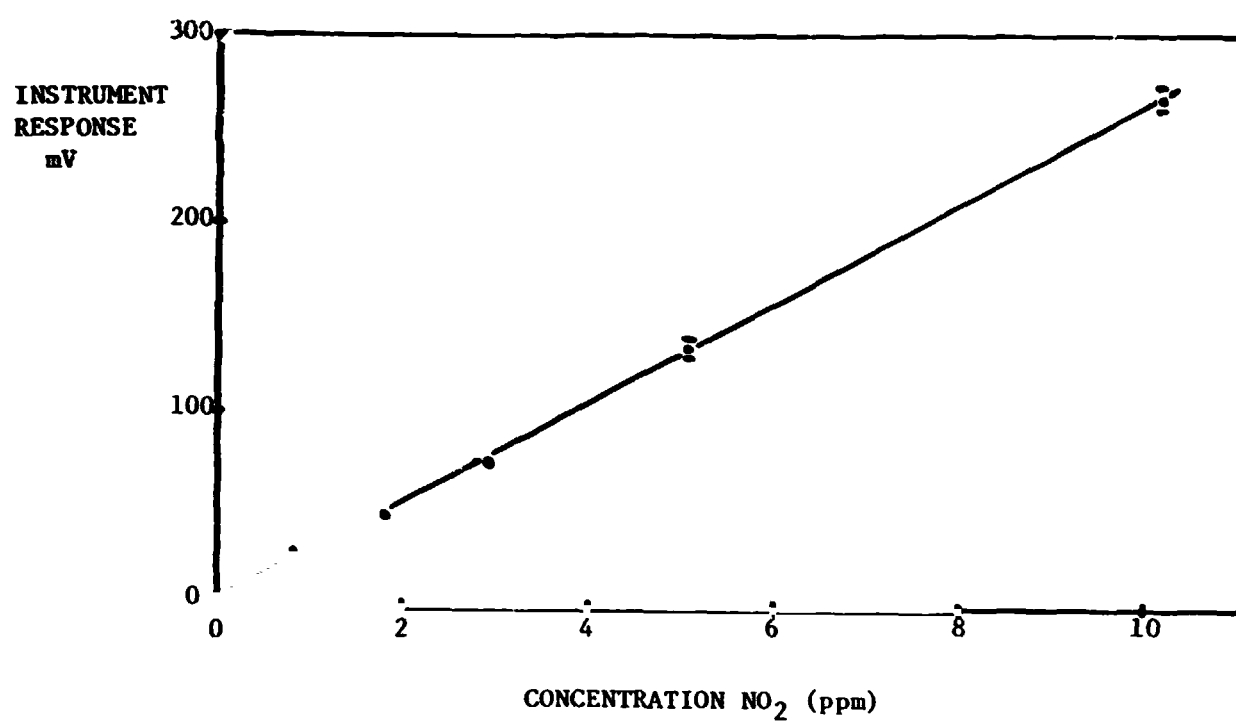
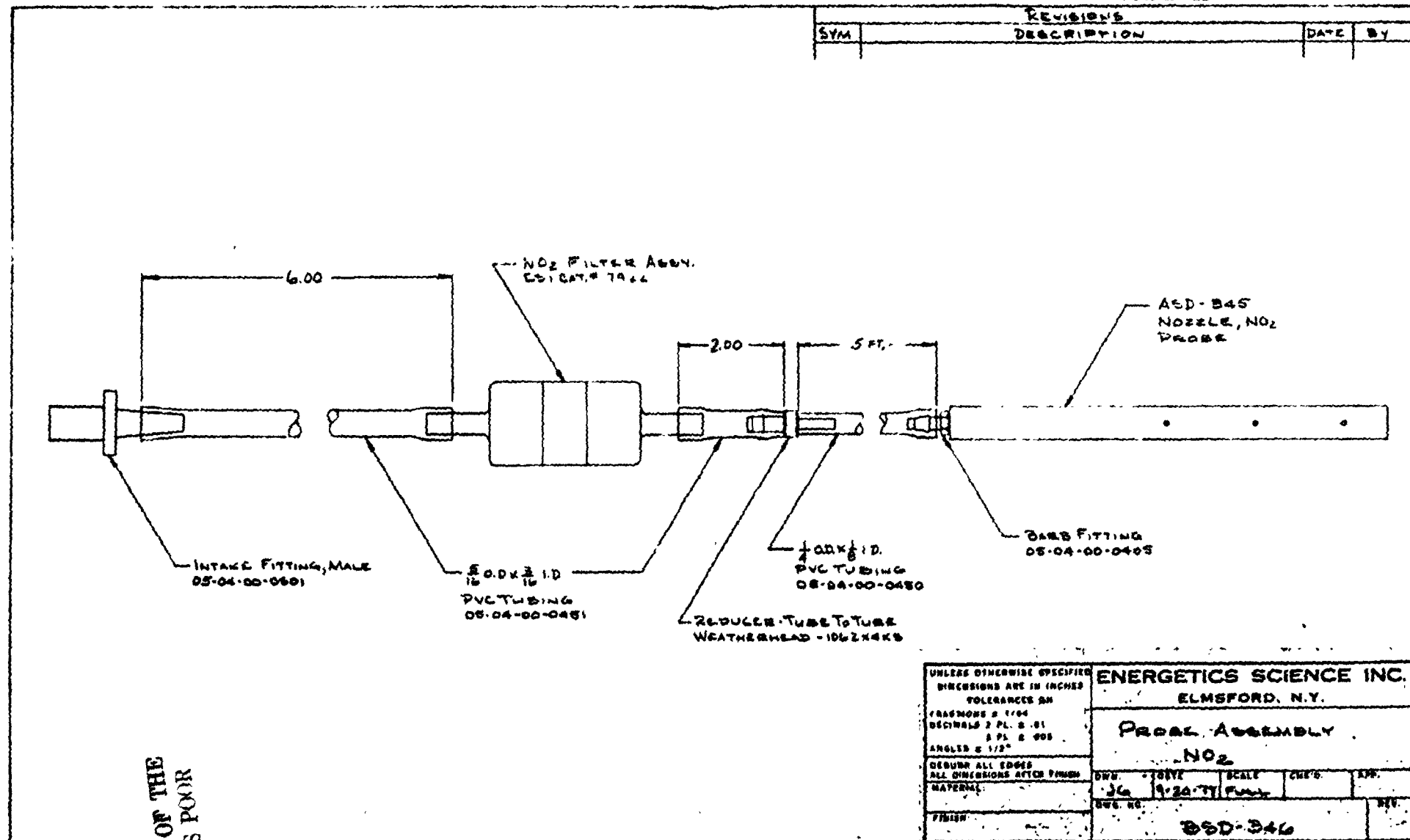


FIGURE 21



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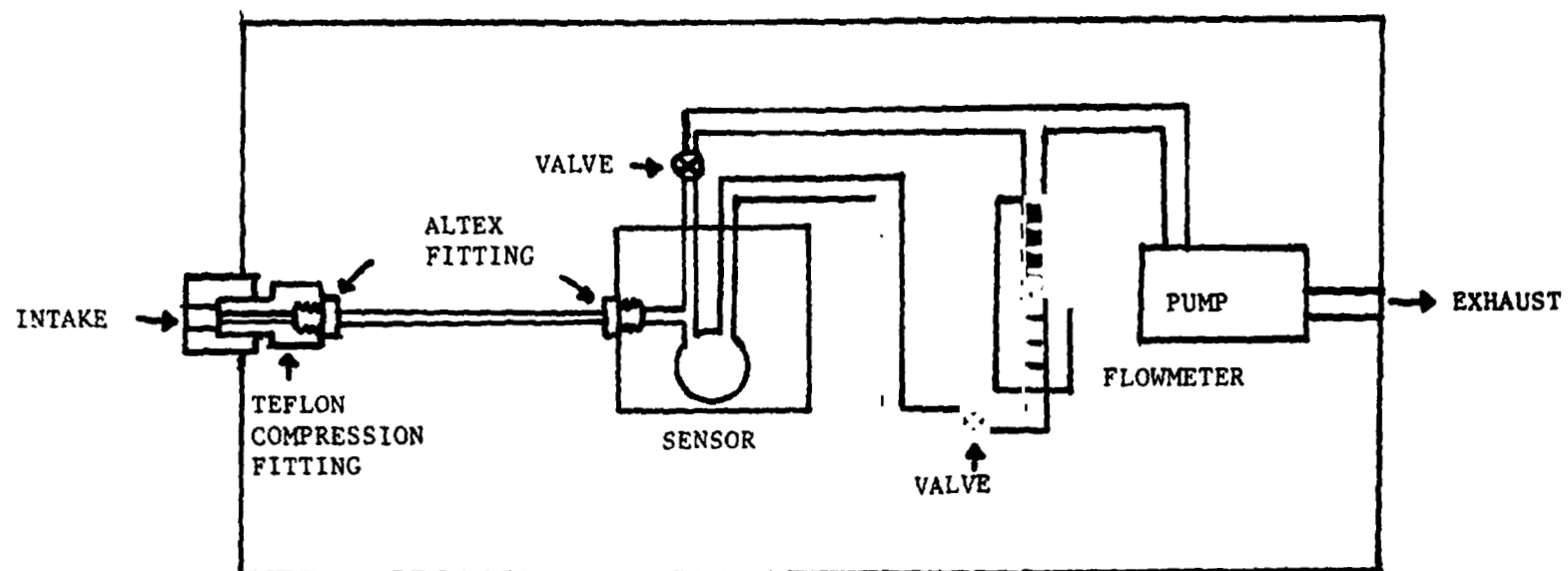


FIGURE 22 SCHEMATIC DIAGRAM OF MODIFIED MMH 7000 SERIES PLUMBING

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FIGURE 23 MODEL 7630 MMH TEMPERATURE DEPENDENCE
S/N 1282

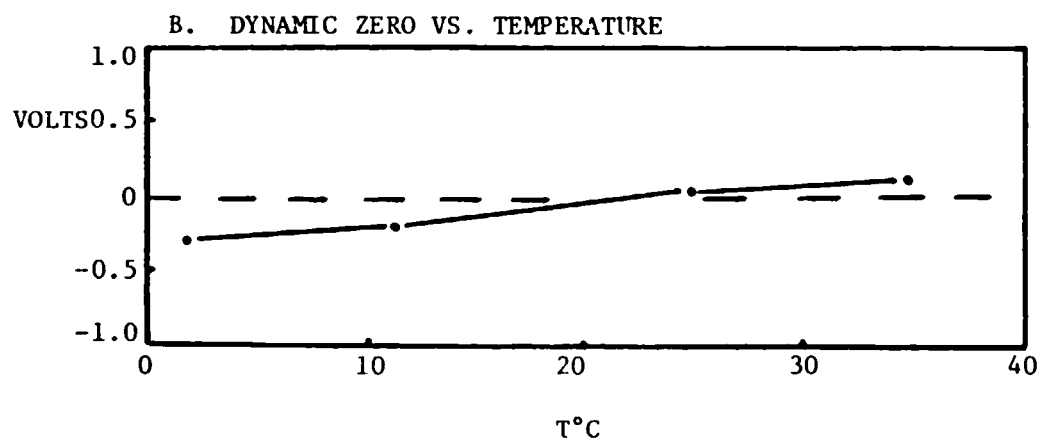
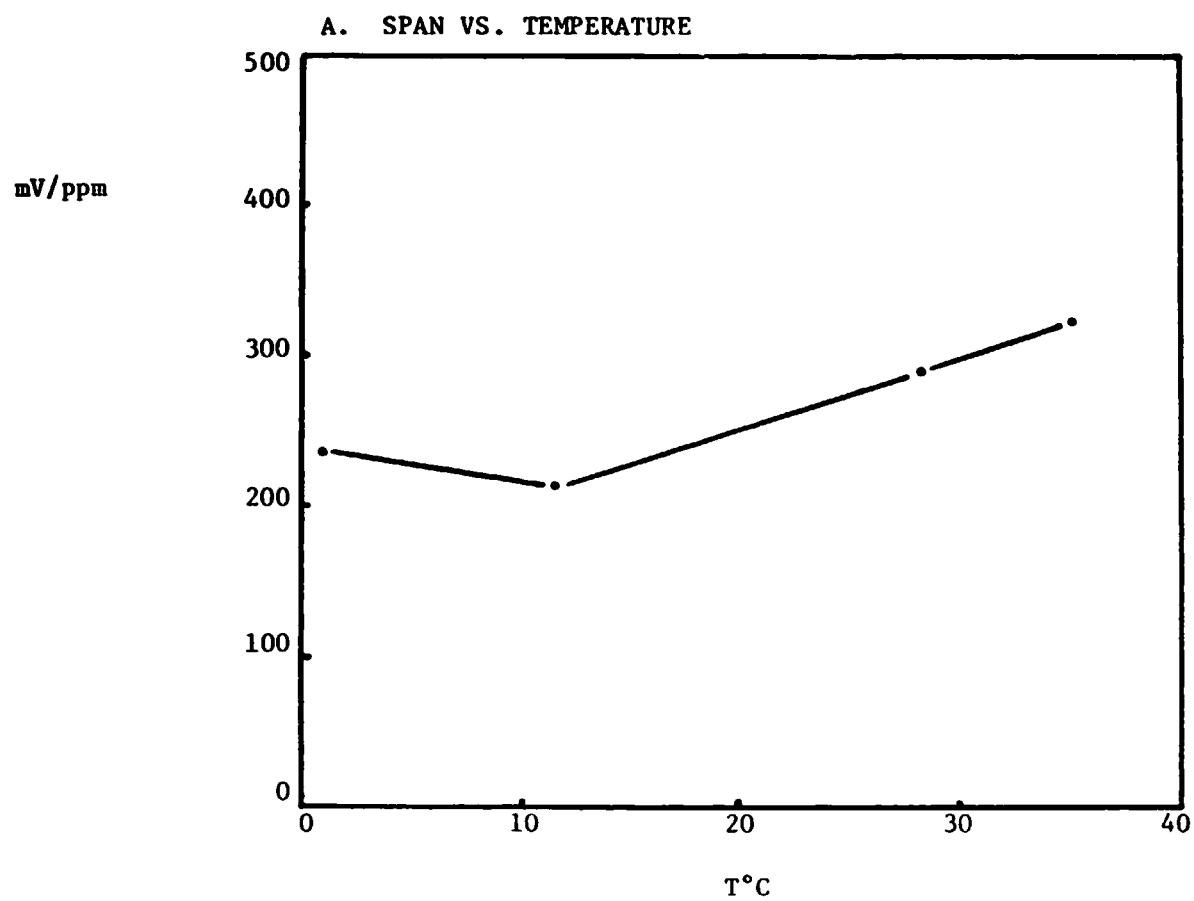
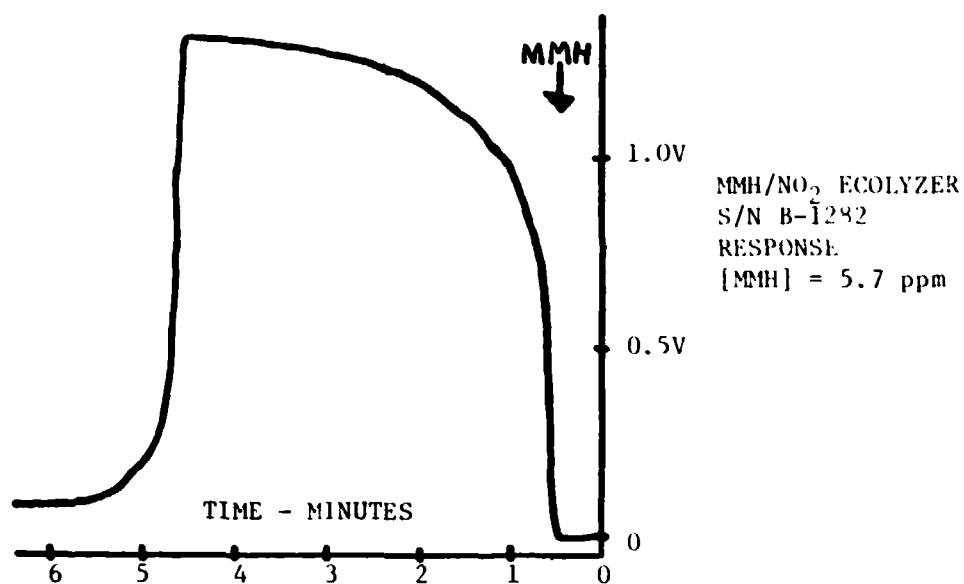
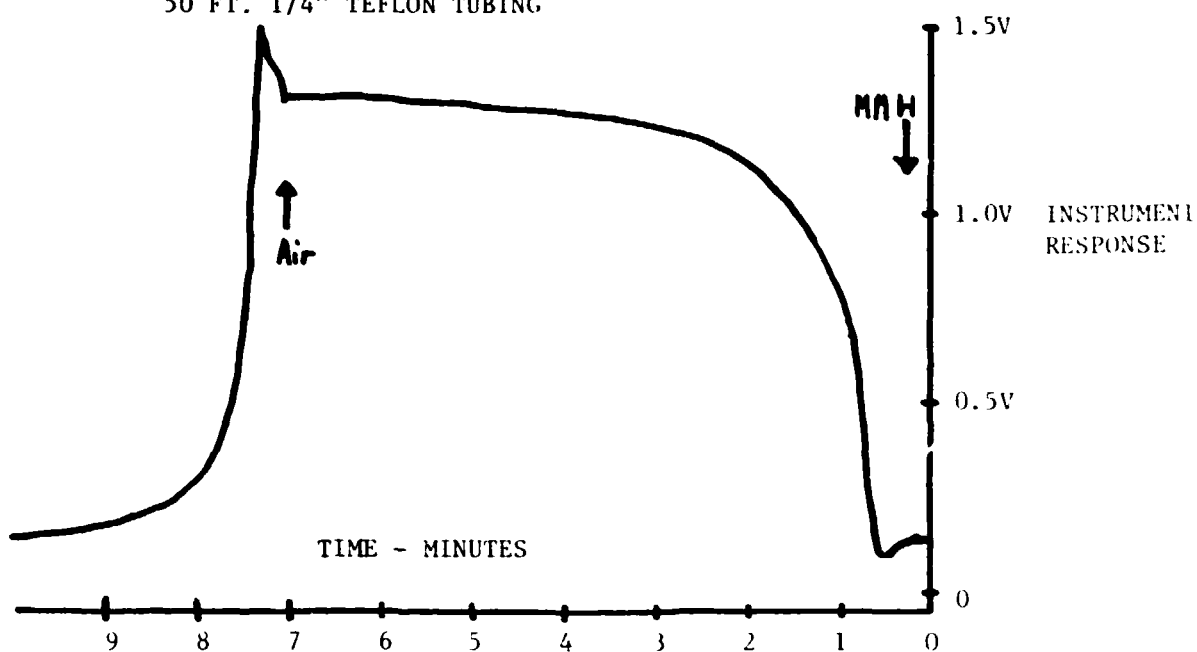


FIGURE 24 EFFECT OF TEFLON TUBING ON MMH RESPONSE

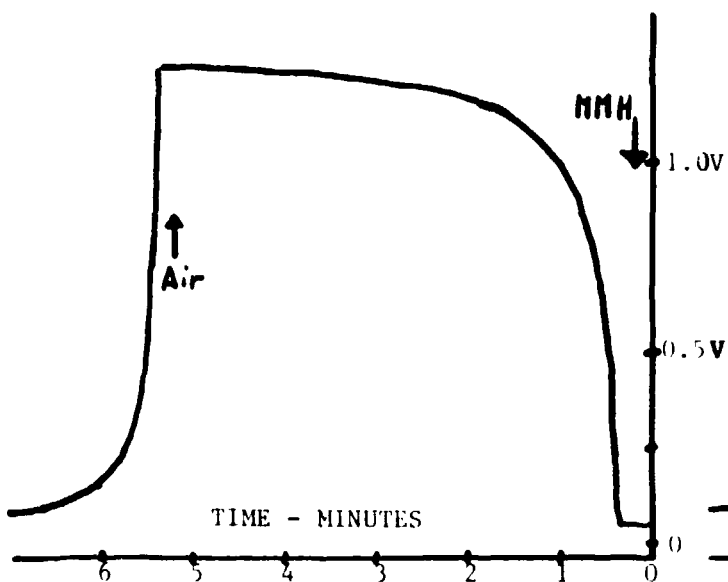
NO TUBING



50 FT. 1/4" TEFLON TUBING



50 FT. 3/16" TEFLON TUBING



50 FT. 1/8" TEFLON TUBING

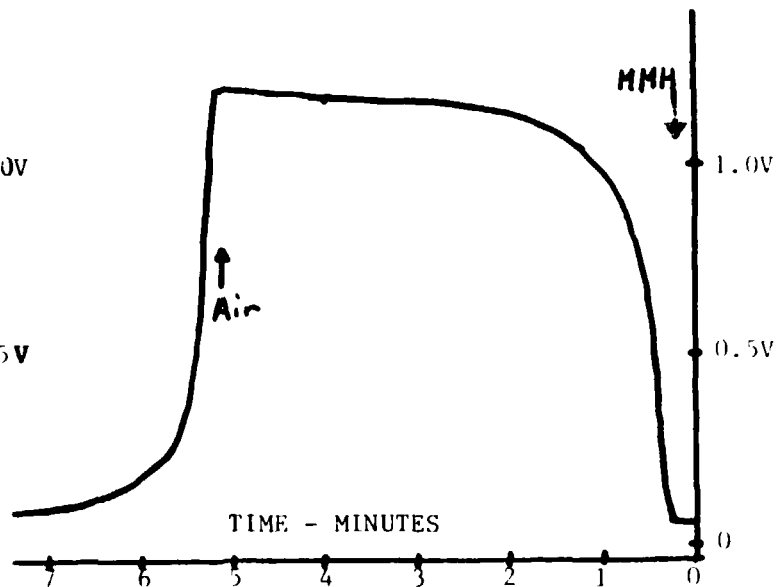


FIGURE 25 EFFECT OF TEFLON TUBING ON NO₂ RESPONSE MODEL 7630 ECOLYZER

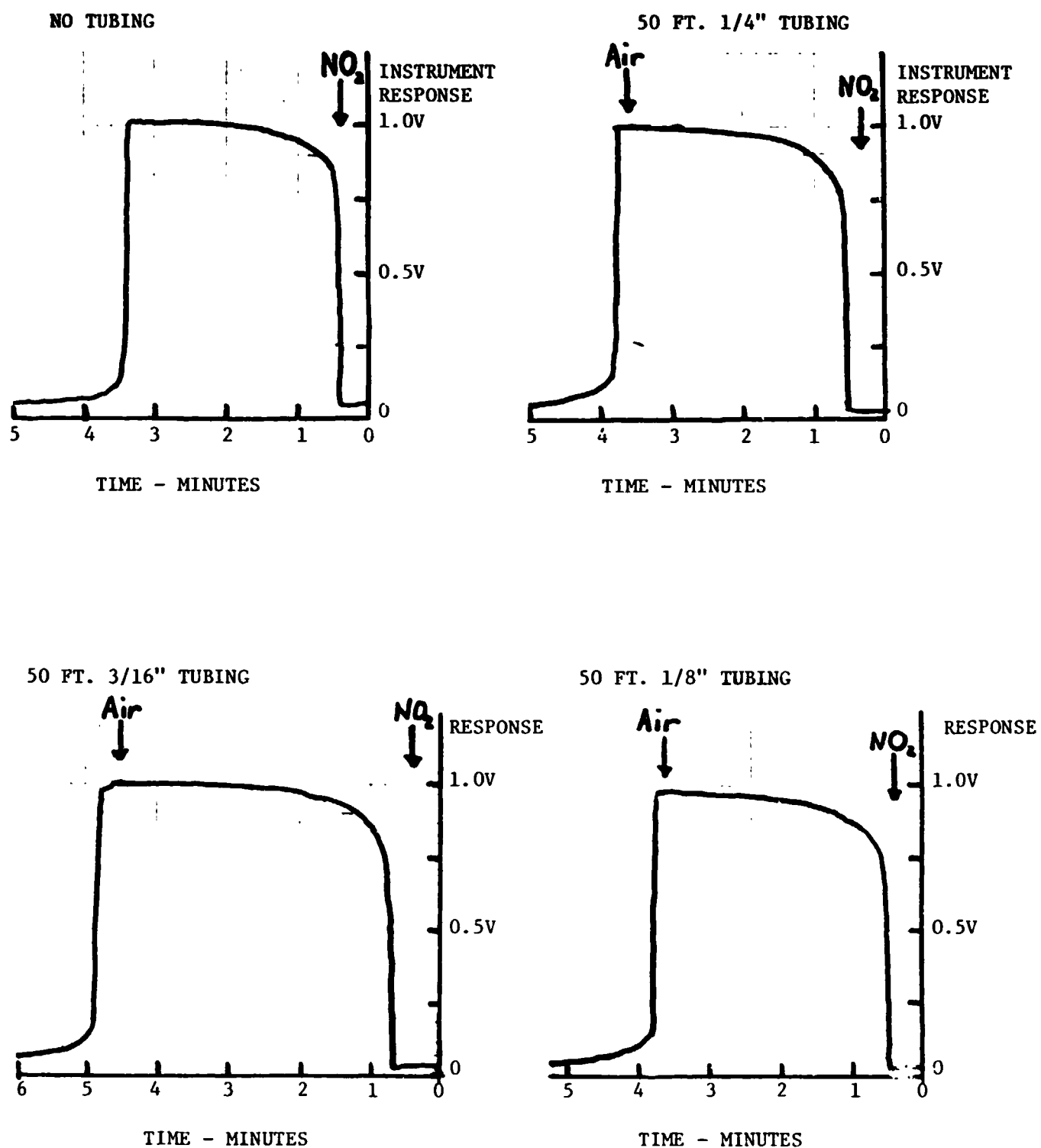


FIGURE 26 UDMH/N₂ STABILITY

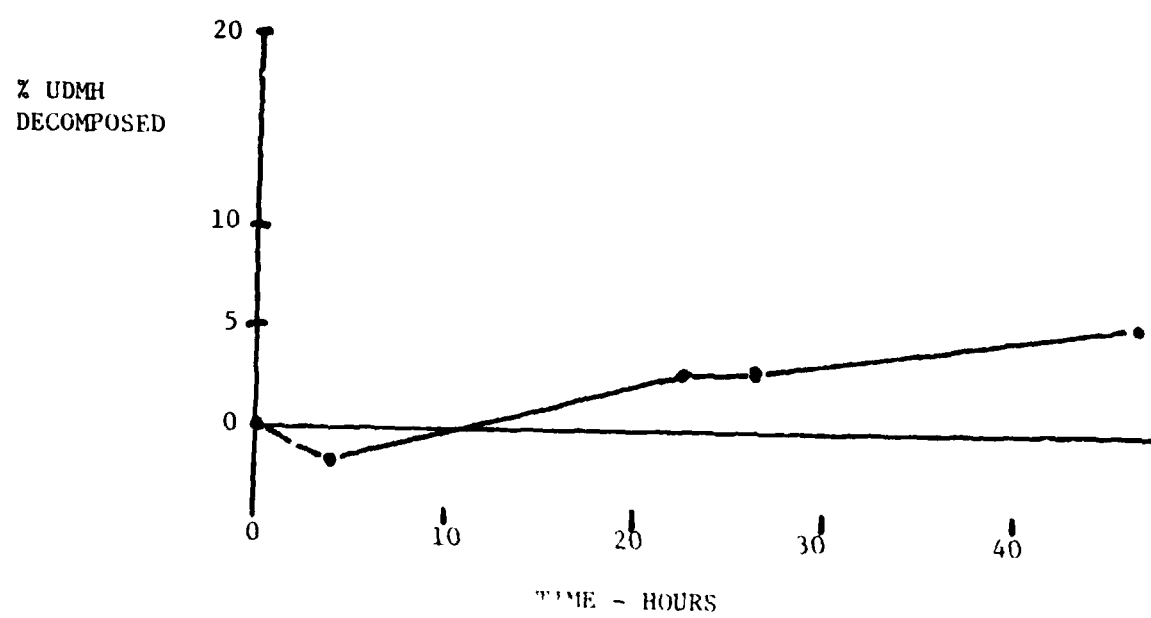


FIGURE 27 COLORIMETRIC CALIBRATION CURVE FOR MMH

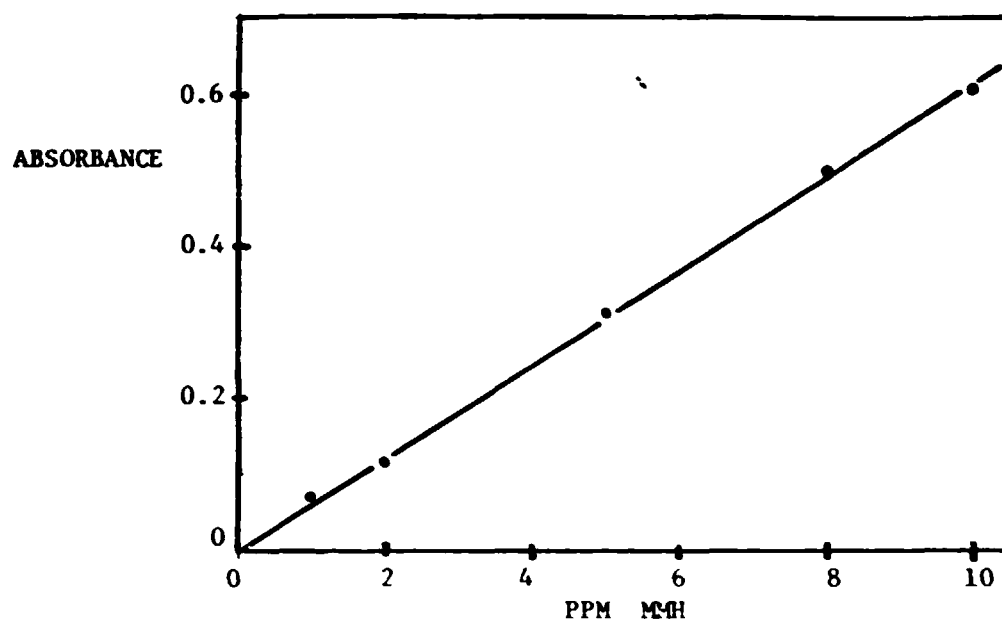


FIGURE 28 COLORIMETRIC CALIBRATION CURVE FOR HYDRAZINE

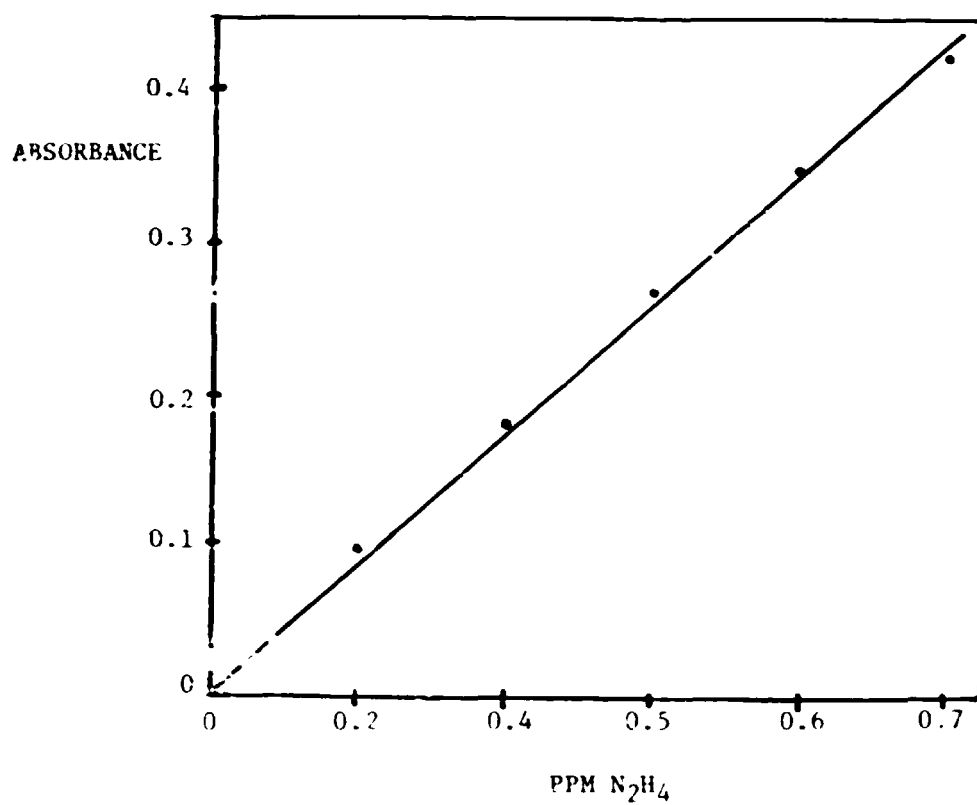


FIGURE 29 COLORIMETRIC CALIBRATION CURVE FOR UDMH

